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Organic Compounds in Organophosphorus Pesticide Manufacturing Wastewaters

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Preliminary survey information on the organophosphorus pesticide industry wastewater streams and analytical methods to monitor levels of organic compounds present in these streams are presented. The identification and quantification of organophosphorus compounds was emphasized, but nonphosphorus chemicals were also included in the survey. A secondary goal of the program was to use the survey information to evaluate the efficiency of various waste treatment processes.

The wastewater from five pesticide plants that produced eight organophosphorus pesticides was sampled. The pesticides were diazinon; methyl parathion; azinphos-methyl and disulfoton; fonofos, phosmet and bensulfide; and EPN.

The 116 compounds identified included organophosphorus pesticides, related organophosphorus esters, organophosphorus acids, volatile organic compounds, thiocarbamate pesticides, triazine herbicides, and miscellaneous extractable process chemicals, by-products, and compounds of unknown origin.

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Organic Compounds in Organophosphorus Pesticide Manufacturing Wastewaters

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ORGANIC COMPOUNDS IN ORGANOPHOSPHORUS PESTICIDE MANUFACTURING WASTEWATERS

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FOREWORD

Nearly every phase of environmental protection depends on a capability to identify and measure specific pollutants in the environment. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Analytical Chemistry Branch characterizes chemical constituents of water and soil.

The toxicity and persistence of pesticides and their decomposition products are problems of major importance to those concerned with environmental quality. In addition to evaluating potential problems associated with the application of pesticides, environmental concern has been directed toward identifying and quantifying specific compounds associated with pesticide manufacturing effluents. This report examines organophosphorus pesticide plant wastes, which are of particular importance because these pesticides are among the most toxic compounds produced in appreciable quantities in the United States.

David W. Duttweiler
Director
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ABSTRACT

The major goals of this program were to develop preliminary survey information on the organophosphorus pesticide industry wastewater streams and to develop analytical methods to monitor levels of organic compounds present in these streams. The identification and quantification of organophosphorus compounds were emphasized, but nonphosphorus chemicals were also included in the survey. A secondary goal of the program was to use the survey information to evaluate the efficiency of various waste treatment processes.

The wastewater from five pesticide plants that produced eight organophosphorus pesticides was sampled. The pesticides were: diazinon; methyl parathion; azinphos-methyl and disulfoton; fonofos, phosmet and bensulide; and EPN. Samples were taken at pre-, mid- and posttreatment locations.

The analytical methodology included extraction and partitioning, gas chromatography with specific element detection, thin-layer chromatography, infrared spectroscopy and gas chromatography/mass spectrometry.

Methods and procedures were developed by analysis of (a) distilled water samples fortified with model compounds and (b) an actual wastewater sample from the azinphos-methyl/disulfoton production plant.

The 116 compounds identified included organophosphorus pesticides, related organophosphorus esters, organophosphorus acids, volatile organic compounds, thiocarbamate pesticides, triazine herbicides, and miscellaneous extractable process chemicals, by-products, and compounds of unknown origin.

The levels of parent pesticides in the final effluents were below 0.005 mg/liter. Oxygen analogs of the pesticides were not a significant degradation product of any of the waste treatment processes. Phosphorothioates and organophosphorus acids were only partially removed by the treatment processes, and were observed at the parts per million levels in some final effluents. Phenylphosphonate esters closely related to the parent pesticides were observed in a final effluent sample at parts per billion levels. Volatile organic compounds were effectively removed by the treatment systems with the exception of one totally enclosed system. One effluent which was disposed in an injection well contained over 150 mg/liter organic disulfides, almost 200 mg/liter thiocarbamate pesticides and over 100 mg/liter organophosphorus acids.

Recommendations were made regarding further work in treatment system evaluation, synergistic toxicity studies of organophosphorus compounds, analytical method development, and the fate of wastewater in injection well systems.

This report was submitted in fulfillment of Contract No. 68-03-2343 by Midwest Research Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period June 30, 1975, to November 29, 1977, and the work was completed as of April 17, 1977.

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The cooperation of the personnel from all five pesticide production facilities is very much appreciated and was necessary for the success of the program.

SECTION 1

INTRODUCTION

The possible hazardous effects of many chemical pollutants have stimulated efforts to identify and quantify specific compounds associated with various industrial effluents. The nature of organophosphorus pesticide plant effluents is of particular importance because organophosphorus pesticides are among the most toxic compounds produced in appreciable quantities in the United States.

The major goals of this program were to develop preliminary survey information on the organophosphorus pesticide industry wastewater streams and develop analytical methods to monitor levels of compounds present in these streams. The identification and quantification of organophosphorus compounds were emphasized, but nonphosphorus chemicals were also included in the survey. A secondary goal of the program was to use the survey information to evaluate the efficiency of various waste treatment processes.

Presented in this report are the following: the conclusions and recommendations resulting from this study; the experimental methods; the selection and sampling of production facilities; and a discussion of results. The results are discussed for each class of compound identified, each production facility, and analytical method development. Appended to this report are nomenclature and structural information for organophosphorus compounds and the mass spectra of the compounds identified that were not contained in the Mass Spectral Search System (MSSS)* at the time of this study.

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* Mass Spectral Search System, ADP Network Services, Cyphernetics Division, Copyright 1975.

SECTION 2

CONCLUSIONS

* The analytical methodology developed and applied in this study was successful in identifying and quantifying organic compounds present in pre-, mid- and posttreatment samples of five organophosphorus pesticide manufacturing plants. The compounds identified were classified as follows: organophosphorus compounds, 47 of them ranging in concentration from 0.01 to 50 mg/liter, including organophosphorus pesticides and oxygen analogs, and organophosphorus esters and acids; volatile (purgeable) organic compounds, 24 of them ranging in concentration from 0.004 to 1,400 mg/liter, including alcohol precursors, process solvents, chlorinated hydrocarbons, alkyl sulfides and disulfides, and miscellaneous compounds; nonpurgeable nonphosphorus compounds, 45 of them ranging in concentration from 0.01 to 120 mg/liter, including triazines and thiocarbamate pesticides, precursors and by-products, and compounds of unknown origin.

* The levels of organophosphorus pesticides in the final effluents were low, generally below 0.005 mg/liter, indicating effective removal by the waste treatment systems that were studied.

* Oxygen analogs of the pesticides were generally not a significant degradation product of any of the treatment processes.

* In general, low molecular weight alkyl phosphates, phosphorothioates and phosphorodithioates were effectively reduced in concentration by the waste treatment systems. Several methyl phosphorothioates actually increased in concentration across the treatment systems, which might be indicative of biomethylation of phosphorothioic acids. Organophosphorus acids were also identified in final effluent samples and appear to be only partially removed by the treatment systems.

* Phenylphosphonates, chlorophenylphosphonates, and phosphonothioates (all of which were involved in only one of the plants studied) were partially removed by the waste treatment system; however, many of these compounds persisted in the final effluent at low levels. It is significant that several of these compounds are not simple alkyl esters but are closely related to the parent pesticides (leptophos and EPN), and are potential cholinesterase inhibitors.

* Volatile (purgeable) organic compounds were effectively removed by the waste treatment systems that were studied; an exception was one plant with a totally enclosed biodegradation system.

* The injection well sample studied contained relatively high levels of organophosphorus acids (over 100 mg/liter), thiocarbamate pesticides (approximately 200 mg/liter), and organosulfur compounds (over 150 mg/liter) after pretreatment by base hydrolysis. This method of waste disposal cannot be evaluated until the fate of this injected wastewater is known.

* The overall analytical methodology was successful in identifying many compounds in the wastewater. However, methods in a few analytical areas should be improved prior to further work on these types of effluents. These areas include: analysis of nonvolatile compounds, preservation of samples, and chromatography of selected pesticides.

SECTION 3

RECOMMENDATIONS

* Although the pesticides were effectively removed by the treatment systems observed, the mechanism of removal, i.e., degradation or adsorption, is unknown. Since solids from biotreatment systems are usually landfilled, the disposal of these solids is a potential problem if they contain adsorbed pesticides. The mechanism of pesticide removal should be determined.

* The rates of hydrolysis of all organophosphorus compounds identified in the final effluents should be determined.

* Individual and synergistic toxicities of all organophosphorus compounds identified in the final effluent should be determined.

* Open aeration ponds should be evaluated as a possible fugitive air emission source for volatile organic compounds.

* Additional methods development should be conducted in the areas of:

- Analysis of nonvolatile compounds by derivatization or alternative procedures such as HPLC.

- Concentration of organic compounds from the wastewater by accumulator columns.

- Preservation of VOA samples, aqueous composites and organic extracts to minimize further degradation and chemical reactions prior to analysis.

- Improved chromatographic systems for selected pesticides, e.g., azinphos-methyl and bensulide.

* The presence of organophosphorus compounds at parts per million levels in the injection well sample is of concern until the ultimate fate of the wastewater is known. The organophosphorus pesticide manufacturers who dispose of wastewater in this manner should be identified. A study of wastewater migration rates and directions should be made to determine the safety of this disposal method in each separate case.

* It is important to verify the identification of the O-alkyl-O-(substituted aryl) phenylphosphonates because of their apparent long-term (> 1 year) persistence and probable high toxicity. These compounds should be synthesized for mass spectral confirmation of identifications that were based on manual interpretations.

* Recommended procedural modifications are described in the Methods Development Section of this report.

SECTION 4

EXPERIMENTAL

The experimental portion of the program is discussed in two sections, sampling and analytical procedures. The sampling section specifies the equipment and procedures used to collect 24-hr composite and volatile (purgeable) organic samples and describes the safety aspects of field sampling. The analytical procedure discussion is divided into six sections which include: extraction and partitioning; gas chromatography (GC); thin-layer chromatography (TLC); frustrated multiple internal reflectance infrared spectroscopy (FMIR); gas chromatography/mass spectrometry (GC/MS); and volatile organic analysis (VOA).

SAMPLING

The goal of the sampling protocol was to obtain contamination-free waste effluent which is representative of both the stage of treatment sampled and of the discharge for an average 24-hr production period. The protocol was designed to provide a 5 µg/liter (ppb) detection limit for parent pesticides in final (treated) effluents. Sampling point selection was based on the following criteria: characterization of major phases of treatment, cooperation of plant personnel, and physical accessibility. The sampling equipment and procedures selected to meet this goal are discussed; safety procedures followed during this sampling are presented at the conclusion of this section.

Equipment

Brailsford Model DU-2 effluent samplers were used to collect the 24hr composite waste samples. The 2-gal. Nalgene sample jug was replaced with a 4-liter glass Erlenmeyer flask. The uptake and delivery tubing was replaced with Teflon tubing. After collection, the effluent was transferred to 32 oz plain amber Saniglass® bottles for shipping and storage prior to analysis. The paper cap-liner was replaced by a Teflon liner. All glassware was washed with Alconox® followed by rinses with tap water, 10% (v/v) HCl, tap water, 1 N NaOH, tap water, acetone and deionized water. The glassware was air-dried and sealed for shipment to the production site.

Grab samples of the waste effluent to be analyzed for volatile (purgeable) organics were taken in 6 ml Pierce Hypo-Vials™ (actual held volume, 11 ml) sealed with Canton Bio-Medical Microseps® F-174 (silicone rubber with Teflon film). The glass vials were put through the same wash cycle as the composite sample bottles and then heated in a muffle furnace at 500°C overnight. When cool, the vials were sealed with Microseps® and tear-away aluminum seals to prevent contamination prior to field sampling. This easily removable closure was replaced with the standard seal after sample collection. The volatile organic vials were kept cool in insulated containers with Divajex Blue Ice® during period of sampling and shipment back to laboratory.

Procedures

A 2-liter sample was collected at each of the selected points. When consistent with selection criteria, the production site's on-line sampling equipment was utilized. In cases when the production facility had no compositor capabilities, effluent was collected at ambient conditions with the Brailsford samplers, in combination with 8-hr grab sampling when necessary. Following the sampling period the wastewater pH was measured and adjusted to 7 with sodium hydroxide or hydrochloric acid. The sample bottles were then packed with Blue Ice® for refrigerated shipment to MRI's laboratories.

Samples for volatile organic analysis were taken at the same locations as the composite samples. At regular intervals over an 8-hr period the presealed vials were opened, filled to overflow, resealed with a minimum of headspace and refrigerated.

Safety

Because of the toxic nature of the compounds under study, care was taken to protect those directly or indirectly involved with the samples. Field crews wore disposable gloves and rubber overshoes as well as safety shoes, glasses and hard hats. All contaminated disposable items (gloves, wipes, broken sample vials, etc.) were closed in plastic bags and placed in the company's toxic waste containers. The glass sample bottles were sealed in plastic bags and carefully packed to avoid damage and/or leakage during shipment.

ANALYTICAL PROCEDURES

The analytical procedures for this program were designed to obtain maximum information about the complex mixtures of organophosphorus compounds expected in pesticide production wastewater.

A general detection limit of 0.005 mg/liter for the parent pesticides in treated effluents was used as guideline for sample volume, extract concentration and instrumental sensitivity. This limit was met for most pesticides and related organophosphorus esters; exceptions included azinphos-methyl and bensulide for which detection limits were higher due to difficulty in eluting these compounds from the chromatographic systems used.

The quantification and detection limits of parent pesticides and most volatile (purgeable) compounds were based on comparisons with authentic standards. Quantification of nonphosphorus extractable compounds was based on comparison of mass spectral total ion current response for a diazinon external standard. Therefore, the concentration estimates for the latter group of compounds (nonphosphorus nonpurgeable) are less accurate than the concentrations determined for the pesticides and volatile (purgeable) compounds and may vary within an order of magnitude. Organophosphorus esters other than the parent pesticides were quantified against authentic standards when they were available; otherwise, they were compared to diazinon standards. If an organophosphorus compound was detected but not identified, it was classified in as much detail as possible including solubility, degree of hydrolysis and chemical class. The general sample fractionation and analysis schemes are graphically outlined in Figures 1 and 2.

The analytical scheme was designed with an emphasis on the identification and quantification of organophosphorus compounds. As outlined in Figure 2, only sample fractions in which organophosphorus compounds were detected would be further analyzed by GC/MS. Only those nonphosphorus nonpurgeable compounds which partitioned into fractions that contained detectable organophosphorus compounds would be detected by mass spectrometry; therefore, the results obtained from this protocol should not be considered a total characterization of organic content of analyzed wastewater.

Specific techniques described in detail in the following sections are: extraction and partitioning; gas chromatography (GC); thin-layer chromatography (TLC); frustrated multiple internal reflectance spectroscopy (FMIR); gas chromatography/mass spectrometry (GC/MS); and volatile organic analysis (VOA).

Extraction and Partitioning (for nonpurgeable compounds)

To aid in the chemical classification of compounds contained in wastewater an extraction-partitioning scheme (Figure 1) was developed to separate compounds into solubility groups: water soluble compounds at pH 7 (Fraction A); organic bases (Fraction D); and neutral water insoluble compounds (Fraction J).

One liter of each sample was adjusted to pH 7 and extracted three times with 200-ml portions of diethyl ether. The water phase was concentrated to not less than 5 ml in a rotary evaporator, yielding Fraction A. The ether phase was concentrated to 50 ml in a Kuderna-Danish (K-D) evaporator and partitioned three times with 25-ml portions of 1% HCl/H_2O. The ether phase was concentrated to 5 ml in a K-D evaporator, yielding Fraction J. The aqueous phase was adjusted to pH 9 and partitioned three times with 50-ml portions of

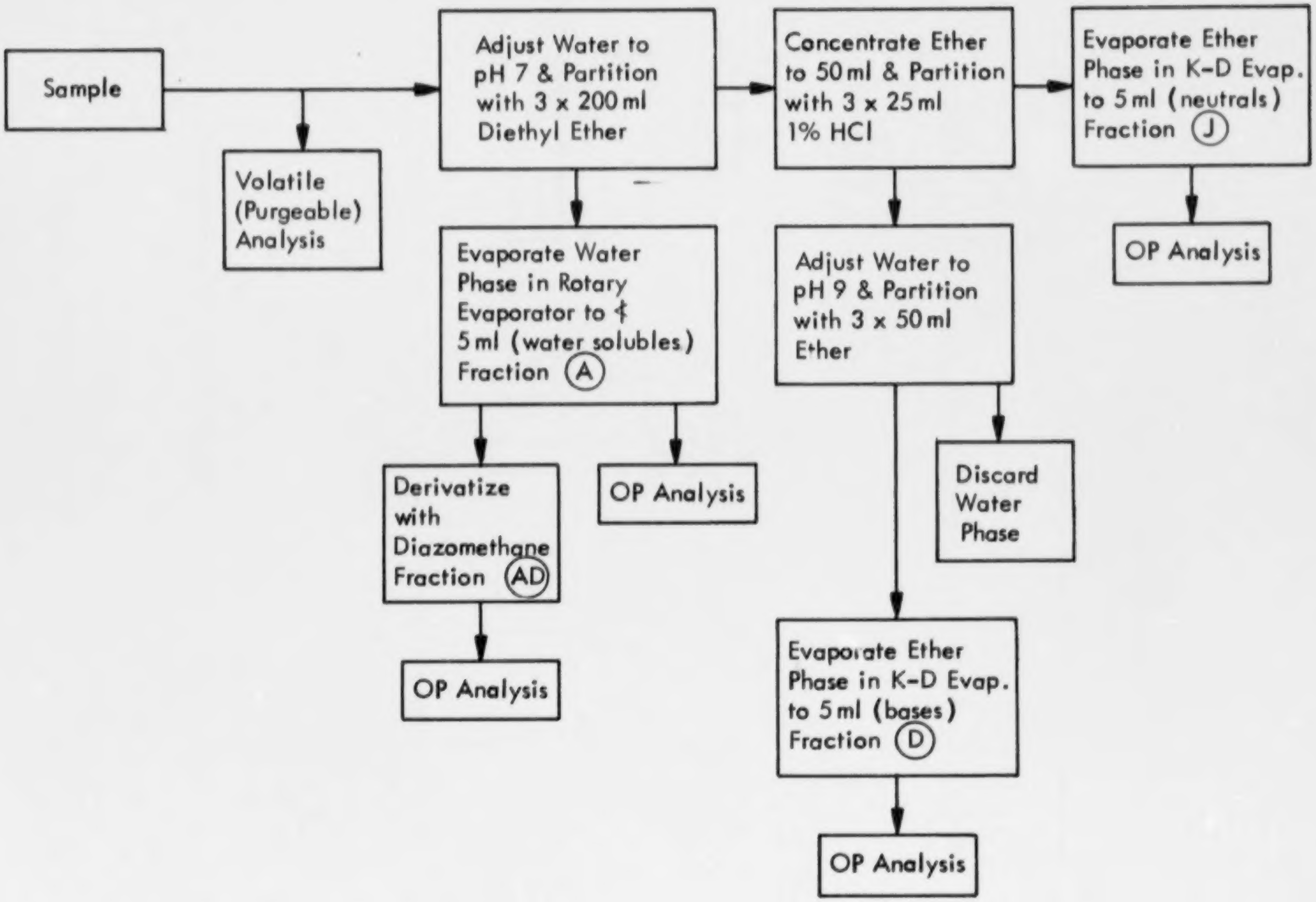
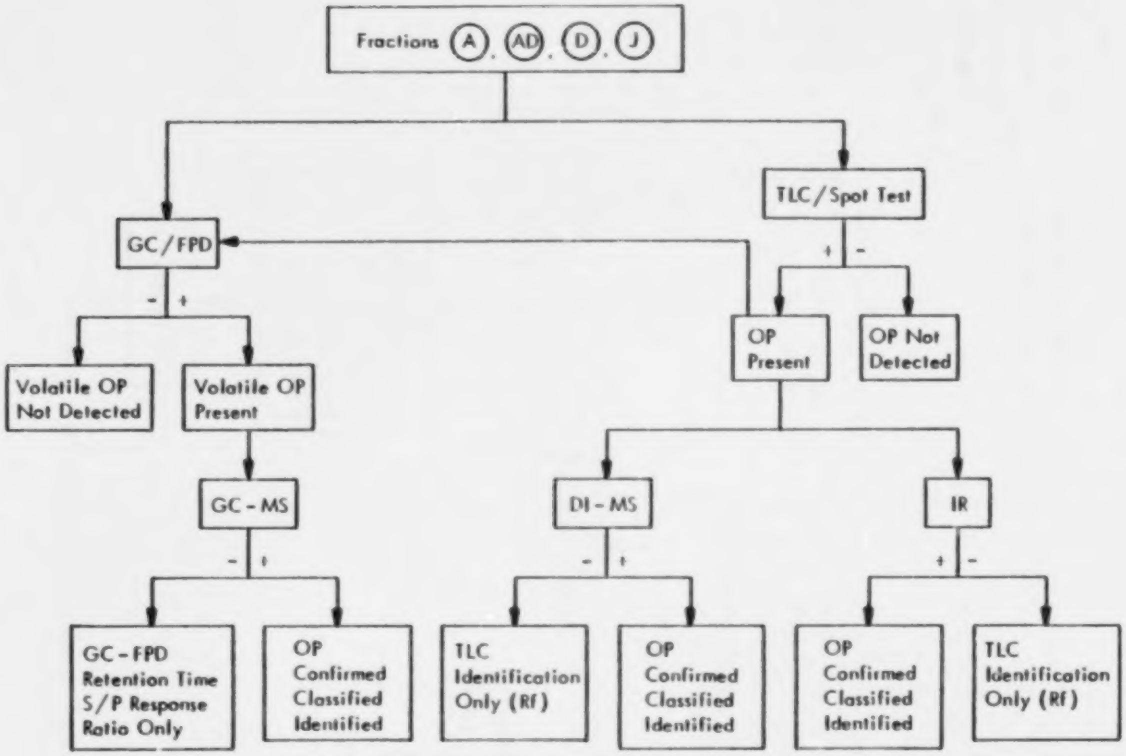

Sample
Volatile (Purgeable) Analysis
Adjust Water to pH 7 & Partition with 3 x 200 ml Diethyl Ether
Evaporate Water Phase in Rotary Evaporator to 5 ml (water solubles) Fraction Ⓐ
Derivatize with Diazomethane Fraction AD
OP Analysis
OP Analysis
Concentrate Ether to 50 ml & Partition with 3 x 25 ml 1% HCl
Adjust Water to pH 9 & Partition with 3 x 50 ml Ether
Discard Water Phase
Evaporate Ether Phase in K-D Evap. to 5 ml (bases) Fraction Ⓓ
OP Analysis
Evaporate Ether Phase in K-D Evap. to 5 ml (neutrals) Fraction Ⓙ
OP Analysis

Figure 1. General sample fractionation scheme.


Fractions (A), (AD), (D), (J)
TLC / Spot Test
GC / FPD
+
-
OP Present
OP Not Detected
Volatile OP Not Detected
Volatile OP Present
GC - MS
DI - MS
IR
GC - FPD Retention Time S/P Response Ratio Only
OP Confirmed Classified Identified
TLC Identification Only (Rf)
OP Confirmed Classified Identified
OP Confirmed Classified Identified
TLC Identification Only (Rf)

LEGEND

TLC - Thin Layer Chromatography
GC/FPD - Gas Chromatography, Flame Photometric Detection
OP - Organophosphorus
MS - Mass Spectrometry
IR - Infrared Spectroscopy
DI - Direct Inlet
S/P - Sulfur/Phosphorus

Figure 2. Analytical scheme for organophosphorus compounds.

diethyl ether. This ether phase was concentrated to 5 ml in a K-D evaporator, yielding Fraction D. Two milliliters of dry methanol was added to the ether solutions of Fractions D and J. Just prior to analysis, the volume of Fractions D and J was adjusted to 2 ml either by evaporation of residual ether or the further addition of dry methanol.

The high concentration of inorganic salts associated with the A fractions led to difficulty in concentrating these water phases to 5 ml. When volumes dropped below 100 ml, copious amounts of solid precipitated, often accompanied by severe frothing. At this point further concentration was halted to avoid problems with gas chromatographic analyses. The exact volumes were recorded and concentration values were calculated accordingly.

Nonvolatile hydrolyzed esters (predicted process degradation products) partitioned into Fraction A. In order to chromatographically analyze for these compounds, a portion of Fraction A was reacted with diazomethane to produce volatile methyl ester derivatives of these organophosphorus (OP) acids.

A 0.5 ml portion of Fraction A was derivatized with diazomethane according to a method reported by C. W. Stanley.[1/] The aqueous solution was taken to dryness under a nitrogen stream. Dry methanol (0.5 ml) was added to the solid residue to extract the organophosphorus compounds from any inorganic salts. The solution was decanted from any remaining material. One drop of 1:1 HCl-ethyl acetate was added to this solution followed by the addition of diazomethane-ether solution until the yellow color persisted. The solution was allowed to stand for a few minutes and then evaporated to less than 0.5 ml under a nitrogen stream. The final volume was adjusted back to 0.5 ml with dry methanol. This solution was designated Fraction AD.

Gas Chromatography (for nonpurgeable compounds)

Fractions A, AD, D, and J were characterized by gas chromatographic (GC) separation coupled with element specific detection (see Figure 2). A phosphorus-sulfur profile was obtained for all sample extracts using flame photometric detection. Samples were submitted for nitrogen-specific alkaline flame ionization detection (AFID) when evaluation of the production and waste treatment processes suggested the usefulness of such a screening. Standard glass columns (6 ft x 2 mm ID) and equivalent temperature programs (allowing for variation of parameter selections of different instrument manufacturers) were used to correlate results with data obtained from GC/MS chromatograms.

Two chromatographic liquid phases (Carbowax 20M-TPA and OV-1) were selected to best cover the range of polarities and volatilities of compounds expected to be detected in sampled wastewaters.

Table 1 lists recommended gas chromatographic parameters for the analysis of intermediately volatile organic compounds. Specific instruments used in all analyses are given in Table 2.

Retention times were calculated relative to diazinon. Approximate concentrations of organophosphorus, sulfur and nitrogen compounds were determined by GC based on element specific response to diazinon external standards.

The GC analysis of samples for two of the five sites required a modification in the standard OV-1 temperature program because the pesticides under study did not elute or chromatographed poorly under the standard conditions. In one case it was only necessary to extend the final hold time period an additional 10 min. However, to obtain well-resolved chromatographic peaks for parathion and its oxygen analog it was necessary to use the temperature program given in Table 3.

Thin-layer Chromatography (TLC)

The sample extracts were developed in three solvent systems. These systems were selected to separate the organophosphorus species anticipated in the effluent samples. The plates were visualized by spraying with a modified molybdate reagent.

Solvent Systems--

The solvent systems and their separation characteristics are summarized in Table 4.

Plates--

The TLC plates (Analtech, Inc., Uniplate, 250 µ, Silica Gel G) were selected on the basis of resolution requirements, low background after visualization, glass thickness, and ability to withstand temperatures required to convert organophosphonates to the visualized orthophosphate species. The plates were developed in 95% ethanol prior to use to reduce the residual background and to improve the reproducibility of standard R_f values.

Visualization Reagents--

Preparation of the visualization reagents was as follows:

Potassium persulfate reagent--Dissolve 2 g of potassium persulfate in 100 ml NH_4OH. This reagent is stable for about 2 weeks.

Ammonium molybdate reagent--Dissolve 2 g of ammonium molybdate in 92 ml of water and add 8 ml of concentrated HCl. This reagent is stable for about 2 weeks.

TABLE 1. GAS CHROMATOGRAPHIC PARAMETERS

Column	Program
3% OV-1 on Supelcoport 80/100 mesh 2 mm ID x 6 ft glass	5 min hold at 120° C, 7.5° C/min programmed temperature, increased to 220° C, 10 min hold at 220° C
5% Carbowax 20M-TPA on Supelcoport 80/100 mesh 2 mm ID x 6 ft glass	5 min hold at 120° C, 5° C/min programmed temperature, increased to 200° C, 10 min hold at 200° C

TABLE 2. INSTRUMENTATION FOR ANALYSIS

Instrument	Analysis
Tracor Model 550 gas chromatograph equipped with dual flame photometric detectors for phosphorus (526 nm filters) and sulfur (394 nm filter)	Phosphorus-sulfur screen
Perkin-Elmer 3920 gas chromatograph equipped with rubidium bead thermionic detector and flame ionization detector	Nitrogen Screen VOA screen and quantitation
Wilks Model 8B Multiple Internal Reflectance spectrophotometer	IR of preparative TLC isolates
Varian/MAT CH-4 magnetic sector mass spectrometer with Tracor 2000-R gas chromatograph Varian/MAT 311-A double focusing mass spectrometer with Varian Aerograph Model 2740 gas chromatograph Varian 620/i minicomputer	Gas chromatography/ mass spectrometry

TABLE 3. GAS CHROMATOGRAPHIC PARAMETERS FOR PARATHION ANALYSIS

Column	Program
3% OV-1 on Supelcorport 80/100 mesh 2 mm ID x 6 ft glass	Initial temperature 100° C, 25° C/min programmed temperature, increased to 220° C

TABLE 4. TLC SOLVENT SEPARATION CHARACTERISTICS

Solvent system	Compounds separated (R_f)
Ethanol 95%	Inorganic P (< 0.2)
	Organic P (> 0.2)
	Mono-alkylated esters
	Di-alkylated esters ↓ (increasing)
	Tri-alkylated esters
Acetone/ethyl acetate (1/1, v/v)	Hydrolyzed esters (0.0)
	Alkyl phosphonates (0.15-0.40)
	Alkyl phosphates (> 0.4)
Methylene chloride	Hydrolyzed esters (0.0)
	Pesticides

"Benzidine" reagent--Dissolve 0.065 g of 3,3',5,5'-tetramethylbenzidine (a noncarcinogenic analog of benzidine) in 8 ml of glacial acetic acid, add 20 ml of water, warm the solution and add slowly 20 g sodium acetate trihydrate. Dilute this solution to 100 ml with water. This reagent is stable for about 2 weeks.

TLC Procedures--

Twenty microliter portions of each extract were applied to TLC plates and developed in each of the solvent systems. The plates were visualized by spraying until wet with potassium sulfate reagent, heating on a hot plate at 235°C for 3 min and allowing to cool. The process was repeated, the plates were sprayed with ammonium molybdate reagent and heated at 180°C until vapors were no longer visible above the plate. The cooled plate was next sprayed with tetramethyl-benzidine reagent. Organophosphonates, organophosphates and thiophosphates, and orthophosphate compounds gave a blue spot on a white background. The detection limit for organophosphorus compounds is 1 to 5 μg.

For preparative TLC, the samples were streaked or spotted across the width of a chromatoplate to obtain sufficient quantities of sample for further studies. After development in the solvent (Table 4) which gave the best separation in the initial development, the plate was divided into two parts: the first was used for visualization of the component bands, the second for recovery of the components at locations corresponding to positive R_f on the visualized plate. Each band was transferred to a disposable micropipet and the compound eluted from the silica gel with several drops of dry methanol. The methanol solutions of these isolated compounds were respotted and developed in the three solvents (Table 4). The resulting three R_f values were then matched against R_f values for standard compounds in the data base, i.e. standards of compounds expected to be detected in the effluent sample.

The isolated phosphorus-containing extracts were characterized further by FMIR, GC/FPD, MS and/or GC/MS (Figure 2). The method used for further characterization was selected on the basis of spot intensity (quantity) and R_f value. For example, a compound with an R_f value equal to zero in acetone/ethyl acetate would be considered nonvolatile and further characterized by FMIR rather than GC.

Frustrated Multiple Internal Reflectance Infrared Spectroscopy (FMIR)

Nonvolatile phosphorus-containing compounds that had been separated and recovered by preparative TLC were characterized by FMIR. The minimum detectable quantity of most organophosphorus esters by FMIR is on the order of 5 μg. The reflectance spectrum of each compound was determined in the range of 4000 to 625 cm^{-1}. Methanol solutions were applied to a 50 x 20 x 2 mm KRS-5 plate for analysis.

FMIR results were used for chemical classification by detecting various functional groups within a molecule and for compound identification by matching unknown spectra with the spectra of standard organophosphorus compounds.

Functional groups and associated absorption bands common to organophosphorus pesticides are listed below.

Functional group	Characteristic absorption bands (cm^{-1})
P=O	1170-1285
POC (C is aliphatic)	990-1080
	770-860
P=S	600-700

Gas Chromatography/Mass Spectrometry (GC/MS)

The standard GC columns and conditions listed in Table 1 were used for GC/MS. The helium carrier gas flow was adjusted so that the retention time of a diazinon standard matched as closely as possible that obtained during the GC/FPD runs.

Mass spectra were taken for all peaks seen on the total ion current (TIC) reconstructed gas chromatograms. Two criteria were used to select a spectrum for interpretation: peak intensity and organophosphorus character. The organophosphorus character was based on a relative retention time window (± 0.05) determined by GC/FPD response and on intensities of characteristic fragments. All mass spectra taken in these windows were chosen as candidates for interpretation, and spectra in these windows with estimated extract concentrations of 200 ppm (approximately 1 ppm in the wastewater sample) as determined by GC/FPD response were given priority.

Spectra from all GC/MS runs were grouped by molecular ion and similar fragmentation patterns, and the best representatives of these groups were subjected to manual interpretation. Spectra of well-resolved compounds were submitted for computer assisted (Biemann Search) mass spectral matching.

Compound identifications were based on one or more of the following: manual interpretation, similarity index matches, comparison of sample spectra with reference spectra from laboratory standards or from the literature, and matches from the Eight Peak Index of Mass Spectra, Mass Spectrometry Data Center, Aldermastun, Reading, U.K. (1970). If an identification was made only by a similarity index or "Eight Peak" match, the identification is considered tentative and the listed compound is indicative of the type or class of compound only.

Volatile Organic Analysis (VOA)

Equipment--

The purging system consisted of a 10 x 180 mm chromatography column with Teflon stopcock and a Ŧ24/42 glass joint at the top. A very fine pore glass frit cylinder, 10 x 1 mm, was press fit into the top of the Teflon stopcock. A glass Ŧ24/42 reducing union to 3 mm was placed at the top of the purging column. A 1/4 in. Teflon union was attached to the 3 mm glass tube at the top of the column. A 3 in. x 1/4 in. stainless steel tube was pressed into the open end of the Teflon union and tightened until gastight. The stainless steel tube was filled with Tenax GC®.

A Bendix Model 10 Flasher was used to thermally desorb the volatile components from the Tenax GC® absorbent.

Procedures--

A number (N) of sealed VOA samples were obtained from each location at regular intervals during 8 hr of the 24-hr sampling period. Equal portions (5/N ml) were withdrawn by syringe from each sealed septum vial and combined to obtain a 5 ml representative composite sample.

This composite was placed in the system described above and was purged with nitrogen at 20 ml/min for 10 min at ambient temperature. The adsorbed volatiles were desorbed at 185°C.

All samples were analyzed by gas chromatography with flame ionization detection (GC/FID) before mass spectral analysis to determine the number of compounds in the sample and estimate the concentrations. If insufficient concentration or too large a concentration for mass spectral analysis was observed, the sample volume was adjusted to obtain the optimum sample for the next purging to be used for mass spectral analysis.

The VOA GC conditions are given in Table 5.

TABLE 5. GAS CHROMATOGRAPHIC PARAMETERS FOR VOA

Column	Program
Chromosorb 101 80/100 mesh 1/8 in. OD x 6 ft stainless steel	4 min hold at 120°C, 4°C/min programmed temperature, increase to 200°C, 8 min hold at 200°C

Quantitation after mass spectral analysis was performed by preparing aqueous standards, purging and determining peak height by FID. Three to five different concentrations were analyzed for each component in the sample. Standards were prepared to bracket the concentration range of that component in the sample. The calibration curves were linear in the concentration range of interest. During work on the protocol sample, it was noted that purging and trapping onto Tenax was not 100% efficient. The method used to quantify the samples assumes reproducible recovery of standards and of standards relative to samples if purging rates and times are carefully controlled. Because linear calibration curves can be obtained by this method, it appears that this is a good assumption.

SECTION 5

SELECTION AND SAMPLING OF PRODUCTION FACILITIES

The discussion of production facilities is divided into three sections: site selection criteria; presampling surveys; and a field sampling summary.

SITE SELECTION CRITERIA

To characterize the organophosphorus pesticide manufacturing effluents on an industry wide basis, the most important selection criteria were total annual production volume, chemical class, toxicity of organophosphorus pesticides produced and type of waste treatment used. After representative compounds (parathion, methyl parathion, diazinon, malathion, phorate, disulfoton, azinphos-methyl, fonofos, bensulide, phosmet, and leptophos) were selected, manufacturers of these compounds were contacted to determine the accessibility of production sites.

PRESAMPLING SURVEYS

Site visits were made to all the consenting facilities to assess the suitability of each location for characterization of the waste effluent before and after treatment. The information needed at each location included the indentification of organophosphorus pesticides produced or formulated; the identification of other organic compounds produced; production methods for the organophosphorus pesticides; production volumes; locations of waste streams; waste treatment technique; location of possible sampling points; and possible problems with the disclosure of identified compounds and their concentrations in the wastewater. Sites were disqualified for the following reasons: refusal of permission to sample, lack of treatment prior to disposal, e.g., ocean dumping, and discontinuation of pesticide production. Facilities that manufacture malathion and phorate did not meet the sampling criteria. EPN was being manufactured at the former leptophos manufacturing facility that was studied, and methyl parathion was being manufactured at the time of sampling the plant that alternates the production of parathion and methyl parathion.

FIELD SAMPLING SUMMARY

Field sampling information is summarized in Table 6.

TABLE 6. FIELD SAMPLING SUMMARY

Date	OP Production sites	Estimated national production in 1974 (million lb)[a]	Sample description	Waste treatment
2-76	Diazinon	12	1. Untreated segregated OP waste 2. After acid destruct, segregated OP waste 3. Discharge to river mixed with non-OP waste	Acid hydrolysis, activated, sludge, aeration, clarifiers
3-76	Methyl parathion	51	1. Untreated acidic waste 2. Combined pH adjusted waste 3. Discharge to city sewer	pH Adjusted, activated sludge aeration, clarifiers
7-76	Disulfoton Azinphos-methyl	10 5	1. Before biotreatment (mixed with non-OP waste) 2. After biotreatment (mixed with non-OP waste)	pH Adjustment, polymer reactor, activated sludge, clarifiers
10-76	Phosmet Fonofos Bensulide	10 3 Not listed	1. Runoff[b] untreated 2. Runoff[b] after aeration 3. Base-treated for deep-well injection	Runoff:[b] pH adjustment, organic skimming, aeration; production waste: base hydrolysis, deep-well injection
11-76	EPN	Not listed	1. Runoff[b] untreated 2. Treated runoff[b] mixed with 35 unknown waste effluents	Aeration, activated sludge, chlorination clarifier

[a] Kelso, G. L., R. Wilkenson, T. L. Ferguson, and J. R. Maloney, "Development of Information on Pesticides Manufacturing for Source Assessment," Final Report, Midwest Research Institute, EPA Contract No. 68-02-1324, July 30, 1976.

[b] Primary production waste disposed by deep-well injection.

SECTION 6

RESULTS AND DISCUSSION

The results are discussed in three major sections: identified compounds; production sites; and methods development.

The identified compounds section contains a list of all compounds identified in this program and a discussion of these compounds by chemical class. The production site section contains a description of each waste treatment facility, the pesticide synthesis methods, a summary of compounds identified at each site, the origin of the compounds identified, and a discussion of the effect of the waste treatment system. The methods development section describes the work carried out on fortified water solutions containing model compounds and on one "protocol" sample taken from the azinphos-methyl/disulfoton production plant.

IDENTIFIED COMPOUNDS

All compounds identified in this study are summarized in Table 7. The identified compounds* and their concentrations are given for each sample location. The compounds are divided into organophosphorus, volatile (purgeable), and intermediately volatile nonorganophosphorus groups. The sample locations are grouped by production site and location of the sample in the waste treatment system (see Table 6). A detailed description of each sample location is given in the Production Site section.

Organophosphorus Compounds

The organophosphorus compounds listed in Table 7 are divided into three groups according to compound class: parent pesticides and oxygen analogs (compounds 1-6); organophosphorus esters (compounds 7-29) and organophosphorus acids (compounds 30-46).

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* The common names of the pesticides are listed in Table 7; the corresponding trade names, chemical names and structures are given in Appendix A, along with general IUPAC nomenclature and structures for organophosphorus compounds.

TABLE 7. CONCENTRATION OF COMPOUNDS IDENTIFIED BY SAMPLE LOCATION

CONCENTRATION (mg/ℓ)

		Diazinon production			Parathion production			Azinphos-methyl and disulfoton production		Fonofos, phosmet, and bensulide production[a/]			EPN production[b/]	
No.	Compound identified	Pre-treatment	Mid-treatment	Post-treatment	Pre-treatment	Mid-treatment	Post-treatment	Mid-treatment	Post-treatment	Pre-treatment	Post-treatment	Injection well	Pre-treatment	Post-treatment
	Organophosphorus compounds													
1	Diazinon	2.0	< 0.006	< 0.006										
2	Methyl parathion				2.0	3.2	< 0.004							
3	Methyl paraoxon				< 0.002	0.01	< 0.002							
4	Ethyl parathion				0.24	< 0.006	< 0.006							
5	Fonofos									0.001	0.001	0.6		
6	EPN												9	< 0.004
7	0,0,0-Trimethyl phosphate				< 0.002	0.80	< 0.002							
8	0,0,0-Triethyl phosphate									0.75	< 0.002	< 0.002		
9	0,0-Diethyl phenylphosphonate												1.2	< 0.004
10	0-(Chloroaminophenyl)-0-methyl phenylphosphonate												0.12	< 0.004
11a	0-(Chlorobromoaminophenyl)-0-methyl phenylphosphonate													0.007
11b	0-(Chlorobromoaminophenyl)-0-ethyl phenylphosphonate												0.22	0.002
12	0,0,0-Trimethyl phosphorothioate				2.7	3.9	4.4							
13	0,0,0-Triethyl phosphorothioate				< 0.002	0.03	< 0.002	< 0.02	0.5					
14	0,0-Dimethyl-0-ethyl phosphorothioate									< 0.002	< 0.002	3.5		
15	0,0-Dimethyl phosphoramidothioate				< 0.002	2.1	2.8							
16	0,0-Dimethyl-N-methyl-phosphoroamidothioate				< 0.002	< 0.002	0.16							
17	0,0-Diethyl ethylphosphonothioate									0.75	0.02	< 0.01		
18	0,0-Dimethyl phenylphosphonothioate												0.04	< 0.004
19	0,0-Diethyl phenylphosphonothioate												0.12	< 0.004
20	0,S-Diethyl phenylphosphonothioate												4	< 0.004
21	0-Methyl-S-ethyl phenylphosphonothioate												0.04	< 0.004

(continued)

TABLE 7 (continued)

		Diazinon production			Parathion production			Azinphos-methyl and disulfoton production		Fonofos, phosmet, and bensulide production[a]			EPN production[b]	
No.	Compound identified	Pre-treatment	Mid-treatment	Post-treatment	Pre-treatment	Mid-treatment	Post-treatment	Mid-treatment	Post-treatment	Pre-treatment	Post-treatment	Injection well	Pre-treatment	Post-treatment
22	O,O-Diethyl chlorophenylphosphonothioate												0.61	< 0.004
23	O-Ethyl phenylphosphonochlorothioate												0.29	< 0.004
24	O-(4-Nitrophenyl)-O-ethyl chlorophenylphosphonothioate												0.3	0.002
25	O,O-Dimethyl-S-methyl phosphorodithioate				2.3	2.3	0.25	5	0.2					
26	O-Methyl-S,S-dimethyl phosphorodithioate				0.02	0.3	0.002	6	< 0.02					
27	O,O-Diethyl-S-ethyl phosphorodithioate				0.09	0.12	0.05							
28	O,O-Diethyl-S-methyl phosphorodithioate				0.80	0.76	0.16	3	0.3					
29	O,O-Diisopropyl-S-methyl phosphorodithioate							< 0.01	< 0.01	4				
30	O,O-Dimethyl-O-hydrogen phosphate[c]				0.07	2.7	< 0.008							
31	O,O-Diethyl-O-hydrogen phosphate[c]	DMQ[d]												
32	O-Ethyl-O-hydrogen ethylphosphonate[c]									< 0.01	< 0.01	12		
33	O-Methyl-O-hydrogen phenylphosphonate[c]												1.4	< 0.004
34	O-Ethyl-O-hydrogen phenylphosphonate[c]												1.4	0.04
35	O,O-Dimethyl-S-hydrogen phosphorothioate[c]				3.5	2.3	0.03							
36	O,O-Dimethyl-O-hydrogen phosphorothioate[c]				1.0	7.0	0.02	25	40	< 0.01	< 0.01	50		
37	O,O-Diethyl-O-hydrogen phosphorothioate[c]	DMQ[d]						< 0.02	6					
38	O,O-Diethyl-S-hydrogen phosphorothioate[c]	DMQ[d]												

(continued)

TABLE 7 (continued)

		Diazinon production			Parathion production			Azinphos-methyl and disulfoton production		Fonofos, phosmet, and bensulide production[a]			EPN production[b]	
No.	Compound identified	Pre-treatment	Mid-treatment	Post-treatment	Pre-treatment	Mid-treatment	Post-treatment	Mid-treatment	Post-treatment	Pre-treatment	Post-treatment	Injection well	Pre-treatment	Post-treatment
39	O-Methyl-O-hydrogen-O-(4-nitrophenyl) phosphorothioate[c]				< 0.008	0.69	< 0.002							
40	S-Ethyl-O-hydrogen phenylphosphonothioate[c]												1.4	< 0.004
41	O-Methyl-S-hydrogen phenylphosphonothioate[c]												0.04	< 0.004
42	O-Ethyl-S-hydrogen phenylphosphonothioate[c]												0.94	0.008
43	O,O-Dimethyl-S-hydrogen phosphorodithioate[c]				4.1	3.1	< 0.008	21	< 0.02					
44	O,O-Diethyl-S-hydrogen phosphorodithioate[c]				2.7	< 0.004	< 0.008	6	4					
45	O,O-Diisopropyl-S-hydrogen phosphorodithioate[c]									< 0.01	< 0.01	50		
46	O,S-Diisopropyl-O-hydrogen phosphorodithioate[c]									0.04	< 0.01	< 0.01		
47	S,S-Dimethyl hydrogen phosphite							< 0.02	0.08					
	Volatiles													
48	Methanol	1,300	1,000	230	98	29	8	0.1	0.1					
49	Ethanol	1,400	1,600	< 0.05				0.3	0.2	1	< 0.05	620	31	< 0.05
50	Propanol									< 0.05	< 0.05	6		
51	Acetone	300	170	16	250	370	0.9	0.5	0.1	18	17	< 0.05		
52	Diethyl ether												22	12
53	Chloroform	140	25	3	0.02	0.02	< 0.01	1.5	1.5	0.6	0.9	< 0.01	0.8	0.6
54	Methylene chloride							0.6	0.5	13	11	< 0.01	< 0.01	6
55	Benzene	1.4	5	2	0.07	0.03	0.005	0.04	0.04	6	3	4	7	5
56	Toluene	3	< 0.05	< 0.05	0.10	0.53	0.009			0.01	0.01	0.6	0.8	0.02
57	Xylene				0.08	0.004	< 0.002						< 0.005	0.01
58	Heptane	60	6	< 0.05										
59	Cyclohexane				< 0.01	< 0.01	0.07							

(continued)

TABLE 7 (continued)

		Diazinon production			Parathion production			Azinphos-methyl and disulfoton production		Fonofos, phosmet, and bensulide production$^{a/}$			EPN production$^{b/}$	
No.	Compound identified	Pre-treatment	Mid-treatment	Post-treatment	Pre-treatment	Mid-treatment	Post-treatment	Mid-treatment	Post-treatment	Pre-treatment	Post-treatment	Injection well	Pre-treatment	Post-treatment
60	1,2-Dichloroethylene													
61	1,2-Dichloroethane							0.4	0.4	0.6	0.5	< 0.01	0.3	0.2
62	1,1,1-Trichloroethane	300	< 0.05	< 0.05				6	6	0.4	0.3	< 0.01	0.3	0.44
63	1,1,2,2-Tetrachloroethane													
64	Dimethyl sulfide							0.02	0.02					
65	Dimethyl disulfide				0.45	0.60	< 0.01			< 0.01	< 0.01	0.08		
66	Methyl ethyl sulfide													
67	Diethyl disulfide									< 0.01	< 0.01	0.3		
68	Ethyl isobutyrate	< 0.005	3	< 0.05						< 0.01	< 0.01	8	0.04	< 0.01
69	Pinacolone													
70	Phenyl acetate							24	10					
71	Chlorobenzene				0.3	0.3	0.76			< 0.01	< 0.01	0.03	0.02	< 0.01
Intermediately volatile nonorganophosphorus														
72	Atrazine	> 10	0.04	NA$^{d/}$										
73	Simazine	0.30		NA$^{d/}$										
74	Propazine	0.06		NA$^{d/}$										
75	EPTC													
76	Vernolate									1.1	0.02	80		
77	Molinate									0.2	< 0.05	58		
78	Pebulate									0.1	0.38	12		
79	Cycloate									< 0.05	< 0.05	0.1		
80	2-Isopropyl-4-methoxy-6-methyl pyrimidine	DNQ$^{d/}$	DNQ$^{d/}$	NA$^{d/}$						0.3	0.07	27		
81	2-Isopropyl-4-ethoxy-6-methyl pyrimidine	1.5	0.08	NA$^{d/}$										
82	2-Isopropyl-6-methyl-4-pyrimidone	> 10	DNQ$^{d/}$	NA$^{d/}$										
83	p-Methoxynitrobenzene				3	1	< 0.01							
84	p-Nitrophenol				< 0.01	9	< 0.01							
85	p-Chlorophenol				3	< 0.01	< 0.01							
86	p-Chloronitrobenzene				0.3	0.4	< 0.01							
87	p-Chloroaniline				0.6	2	2							
88	Hexachlorobenzene				< 0.01	< 0.01	0.1							
89	Diphenyl disulfide													
90	1-Thiol diethyl disulfide									< 0.05	< 0.05	42		
91	1-(Methyl mercapto)-									< 0.05	< 0.05	4		
	diethyl disulfide									< 0.05	< 0.05	120		
92	Phenyl ethyl disulfide									< 0.05	< 0.05	0.4		

(continued)

TABLE 7 (continued)

		Diazinon production			Parathion production			Azinphos-methyl and disulfoton production		Fonofos, phosmet, and bensulide production[a]			EPN production[b]	
No.	Compound identified	Pre-treatment	Mid-treatment	Post-treatment	Pre-treatment	Mid-treatment	Post-treatment	Mid-treatment	Post-treatment	Pre-treatment	Post-treatment	Injection well	Pre-treatment	Post-treatment
93	m-Dichlorobenzene												0.28	< 0.005
94	p-Dichlorobenzene												1.3	< 0.005
95	Trichlorobenzene												0.02	< 0.005
96	2,4-Dichlorophenol												0.01	< 0.005
97	Ethyl isothiocyanate	DNQ[d]		NA[d]										
98	N-Cyanodimethylamine	DNQ[d]		NA[d]										
99	4,4-Dimethyl-2-penten-2-al[e]							2	0.1					
100	Alpha terpineol[e]							0.3	0.03					
101	Terpinol[e]							0.1	< 0.02					
102	6-Cyclohexylhexan-1-ol							< 0.02	0.06					
103	Secondary butyl iodide[e]							< 0.02	0.3					
104	Methyl tridecyl octonate[e]							0.09	0.03					
105	2,2-Dimethyl propanoic acid[e]							< 0.02	0.08					
106	p-Chlorobenzamide							0.01	< 0.02					
107	Diethyl aniline									< 0.05	< 0.05	0.1		
108	Pyrrolizidine[e]									15	< 0.05	< 0.05		
109	Methyl palmitate[e]									0.6	< 0.05	< 0.05		
110	Methyl oleate[e]									0.3	< 0.05	< 0.05		
111	Methyl N-tetradeconate[e]									0.1	< 0.05	< 0.05		
112	Cyclohexanol									< 0.05	< 0.05	4		
113	Biphenyl												2	< 0.01
114	Cresol homolog[e]												0.01	< 0.005
115	2-Chlorobiphenyl												0.01	< 0.005
116	Diisobutylphthalate												0.01	< 0.005

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a/ Pretreatment and posttreatment samples were surface water runoff from the production area; the injection well sample was process wastewater.

b/ Both samples were surface water runoff from the production area. Process wastewater is deep well injected off site.

c/ Identified as the methyl ester of the indicated compound.

d/ DNQ indicates a compound was detected but not quantified; NA indicates a sample was not analyzed.

e/ The identification is based on a similarity index match or on the Eight Peak Index of Mass Spectra, 1st ed., Mass Spectrometry Data Center, Aldermaston, Reading, UK (1970), and not on a match with a full reference spectrum. The identification is unconfirmed and should be considered tentative.

The parent pesticides were detected in pretreatment and midtreatment samples. Pesticide concentrations in final effluents were below the detection limit (~ 0.002 mg/liter). The injection well sample did have detectable levels of fonofos but this sample is not considered a final effluent. Gas chromatographic methods were not successful for azinphos-methyl, phosmet and bensulide, therefore detectin limits of these pesticides were much higher (~ 1 mg/liter), and none of them were identified in any sample. (Bensulide was tentatively identified by TLC in the pretreatment sample.) The oxygen analogs of the pesticides were expected products of the waste treatment systems. Identification of the oxygen analogs is important because of their increased toxicity over the parent pesticide. Methyl paraoxon, the only compound of this type detected, was found in a midtreatment sample but not in the final effluent. Diazoxon, ethyl paraoxon, and fonofoxon were not detected at low parts per billion levels. Standard solutions of these compounds were chromatographed with the sample from the corresponding production sites. Extracted ion current plots were obtained from the GC/MS data for these compounds to establish detection limits at low parts per billion levels. The absence of parent pesticides and their oxygen analogs in final effuents indicates that the five waste treatment systems studied are effective in the removal of these compounds.

Organophosphorus esters (compounds 7-29, Table 7) are either formed as by-products during the synthesis process or during the waste treatment process by solvolysis with alcohols. Phosphate and phosphonate esters (compounds 7-10) were not detected in the final effluents indicating their instability. Phosphorothioate esters (compounds 12-16) appear to be stable in the waste treatment systems studied. Compounds 12, 13, 15, and 16 increased in concentration across the waste treatment systems. This increase might be due to methylation of organophosphorus acids by the biomass treatment. The high water solubility, observed increase in concentration across the waste treatment system, and possible toxic potentiation of the phosphorothioate esters[2/] are of concern for this class of compounds. Although phenylphosphonothioate esters (compounds 18-24) decreased, they were detected in the final effluent (all from the EPN production plant). Of particular significance is that several of the nonhydrolyzed phenylphosphonates and phenylphosphonothioates (compounds 11a,b, 23 and 24) that were detected in the final effluents were not simple alkyl esters. These compounds are probably the most toxic compounds detected in the final effluents. Phosphorodithioate esters (compounds 25-29) were also detected at decreasing concentrations across waste treatment systems. The efficiency of removal is not as high as that for the parent pesticides. Phosphorodithioates have also been indicated as potentiators in toxicity studies and may be of concern in the final effluents.

Organophosphorus acids (compounds 30-46) are formed by the hydrolysis of the parent pesticides and other alkylphosphorus esters. The phosphorodithioate acids (compounds 43-46) are also precursors for pesticide synthesis. Few acid hydrolysis rates have been reported; however, the hydrolysis from the ester to the monoacid is generally faster than the hydrolysis from the monoacid to the diacid. Therefore, the monoacids have moderate stability in aqueous solutions. Four acids (compounds 35-37, and 44) were detected in posttreatment samples; three others (compounds 32, 36, and 45) were detected at 10 to 50 ppm levels in the injection well sample. Although these compounds are not considered cholinesterase inhibitors, their potentiation effects are not known. Because of the levels at which some of the acids were present, the synergistic toxicity of these compounds should be determined. O-Methyl-O-hydrogen(4-nitrophenyl) phosphorothioate (compound 39), which results from the hydrolysis of the methoxy group from methyl parathion, was identified in a midtreatment sample. This product is unexpected because the usual degradation route is a nucleophilic attack on the phosphorus atom which results in the loss of the most acidic leaving groups, i.e., the 4-nitrophenyl group. The analogous acids of other pesticides were not identified but this observed degradation pathway for other pesticides should be studied.

Volatile Compounds

The discussion of volatile compounds as listed in Table 7 is divided into four groups according to chemical class: alcohol precursors (compounds 48-50); production solvents (compounds 51-59); chlorinated hydrocarbons (compounds 60-63); alkyl sulfides and disulfides (compounds 64-67); and miscellaneous (compounds 68-71).

The alcohol precursors methanol, ethanol and propanol were expected compounds in the wastewater. These compounds are water soluble, polar and generally resistant to the waste treatment techniques (ethanol was greatly reduced at two plants).

The production solvents (compounds 51-59) are generally volatile materials and are effectively removed by the waste treatment systems. The method of removal is likely to be vaporization in open aerated treatment basins. Those compounds identified in the azinphos-methyl/disulfoton production wastewater are exceptions. Little or no decrease in concentration was observed because the system is enclosed between the midtreatment and posttreatment sampling locations. The biological treatment had no effect on these solvents.

The origin of the chlorinated hydrocarbons (compounds 60-63) is unknown. These identified compounds are not apparent precursors, by-products, or solvents for organophosphorus pesticide production. A treatment system with good aeration is effective in removing the compounds, as indicated by the decrease in trichloroethane (compound 62) across the diazinon treatment system.

Alkyl sulfides and disulfides (compounds 64-67) are by-products from organophosphorus synthesis. The waste treatment systems are effective in removing these compounds. The injection well sample had significant levels of diethyl disulfide which may be useful in tracking the fate of this wastewater discharge.

The origin of the miscellaneous volatile compounds (68-71) is unknown except for chlorobenzene which is a precursor for methyl parathion production, and was present at a moderate level (0.7 mg/liter) after treatment. The other compounds were identified from MSSS Biemann searches with low similarity index matches and their identification is considered only tentative.

Intermediately Volatile (Nonpurgeable) Nonorganophosphorus Compounds

The compounds as listed in Table 7 are discussed in three groups: nonorganophosphorus pesticides (compounds 72-79); expected precursors and synthesis by-products (compounds 80-96); and compounds of unknown origin (compounds 97-116).

Triazines (compounds 72-74) and thiocarbamate pesticides (compounds 75-79) were detected in the samples taken from the organophosphorus waste treatment systems. These compounds were also produced at the sites that were studied. The final effluents had low or undetectable levels of thiocarbamate pesticides except molinate (compound 77). The final effluent of the diazinon production site was not monitored for triazine herbicides. The injection well sample had significant amounts of the thiocarbamate pesticides and may be reason for concern until the ultimate fate of this wastewater is known.

Nonorganophosphorus precursors and synthesis by-products (compounds 80-96) were effectively treated in the systems studied. _p_-Chloroaniline (compound 87) was an exception, but it is an expected biodegradation product of _p_-chloronitrobenzene (compound 86). Hexachlorobenzene (compound 88) was also observed in a final effluent in moderate concentration (0.1 mg/liter) but was not observed in the pre- and midtreatment samples. High levels of disulfide compounds were identified in the injection well sample, and were probably responsible for its strong odor.

Concentrations of nonorganophosphorus compounds of unknown origin (compounds 97-116) were generally decreased by the wastewater treatment systems. Each compound was identified from a MSSS Biemann search and had a low similarity index match. Therefore, the identification of these compounds is only considered tentative. The listed compound should be considered representative of a compound class rather than a verified compound identification.

Priority Pollutants Identified

Table 8 lists the priority pollutants* that were identified, along with their location in the treatment system and number of times the compounds were

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* Those compounds listed in "Sampling and Analysis for Screening of Industrial Effluents for Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, Revised April 1977.

TABLE 8. PRIORITY POLLUTANTS DETECTED IN PHOSPHORUS- AND NITROGEN-CONTAINING PESTICIDE WASTEWATER SAMPLES

Compound	Compound No. in Table 7	Number of times identified in pretreatment	Number of times identified in midtreatment	Number of times identified in final effluent
Benzene	55	4	4	5
Chlorobenzene	71	2	1	1
Hexachlorobenzene	88	0	0	1
1,2-Dichloroethane	61	2	2	2
1,1,1-Trichloroethane	62	1	1	1
1,1,2,2-Tetrachloroethane	63	0	1	1
Chloroform	53	4	4	3
1,3-Dichlorobenzene	93	1	0	0
1,4-Dichlorobenzene	94	1	0	0
2,4-Dichlorophenol	96	1	0	0
Methylene chloride	54	1	2	2
4-Nitrophenol	84	0	1	0
Toluene	56	4	2	3
1,2-Dichloroethylene	60	2	1	3

identified; concentrations are given in Table 7. These compounds were identified using the analysis protocol developed for this study and not the recommended priority pollutant protocol (developed March 1977). Therefore, the list of priority pollutants given in Table 8 should not be considered complete.

PRODUCTION SITES

The wastewater treatment systems for five organophosphorus production sites producing eight organophosphorus pesticides were studied. Each production site is discussed individually in this section as follows: diazinon production; parathion production; azinphos-methyl and disulfoton production; fonofos, phosmet and bensulide production; and EPN production. The discussion of each site includes the wastewater treatment system and sampling locations; pesticide synthesis methods; compounds identified at each sampling location; and a discussion of each compound's origin and persistance across the waste treatment system.

Diazinon Production

Wastewater Treatment System--

The wastewater treatment system is shown schematically in Figure 3. The wastewater from the diazinon production unit enters the acid destruct holding

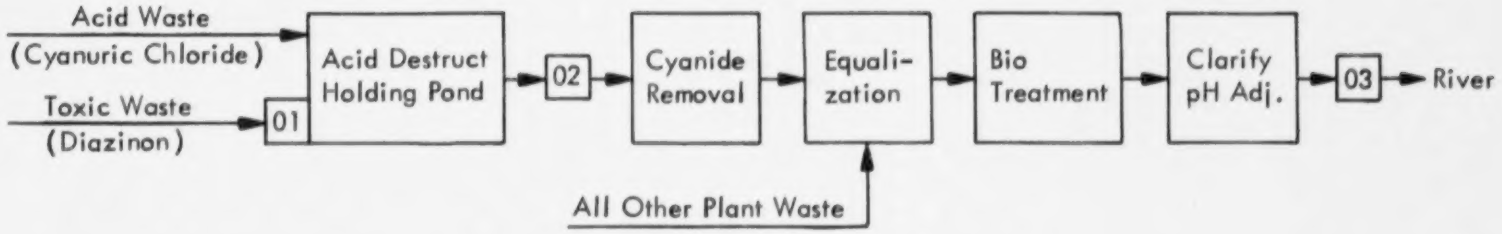

Acid Waste
(Cyanuric Chloride)
Toxic Waste
(Diazinon)
01
Acid Destruct Holding Pond
02
Cyanide Removal
Equalization
All Other Plant Waste
Bio Treatment
Clarify pH Adj.
03
River

Figure 3. Wastewater treatment sampling points for diazinon production.

pond. This wastewater stream does not include cooling water from the diazinon production and therefore is not diluted. The total flow for the 24-hr sampling period at the pretreatment sample point (01 on Figure 3) was 91,560 gal. at a pH of 10.6. The acid destruct pond was at pH 1.0. As indicated in Figure 3, an additional wastewater stream labeled "Acid Waste" (cyanuric chloride) also enters the acid destruct holding pond. The pretreatment sample was taken from an in-line flow dependent composite sampler used by the production site for their own samples.

The diazinon wastewater has a several day hold-up in the acid destruct pond. Diazinon is relatively unstable (T_{50} at pH 3.1 is 12 hr)[3/] to acid hydrolysis when compared to other dialkyl phosphorothioates. The acid treatment is intended to be the primary destruction method for diazinon. The acid hydrolysis of diazinon minimizes the formation of diazoxon.

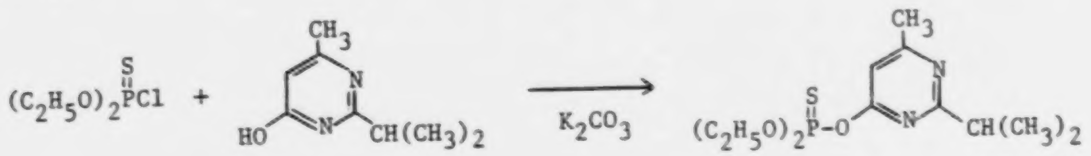
The effluent from the "Acid Destruct Holding Pond" was sampled at Location 02 (Figure 3). The total flow for the sampling period was 250,000 gal. This resulted in about a threefold dilution of the "Toxic Waste" (diazinon) by the "Acid Waste" stream.

Cyanide, when present, is removed by caustic chlorination, the pH is adjusted to 6.5, and wastewater from other production units is mixed before the combined waste stream enters an aerobic biological treatment system. The water is then clarified and pH adjusted before river discharge. The "Posttreatment" sample (03) was taken at this location. The 24-hr composite sample was taken from an in-line flow proportional sampler. The flow volume for the final effluent during 24-hr sampling was 1.4 million gallons. This implies a 15-fold dilution of the "Toxic Waste" (diazinon) stream.

The waste treatment system for diazinon wastewater is designed to remove material by the following method: acid hydrolysis, neutral hydrolysis, biological degradation, adsorption onto biomass, and vaporization. Additionally, compounds detected at low levels in the pretreatment (01) sample may be below the detection limits in the final effluent due to the dilution resulting from additional wastewater inputs into the treatment system.

Pesticide Synthesis Method--

The synthesis of diazinon is a simple condensation reaction between 0,0-diethyl phosphorochlorothioate and 2-isopropyl-6-methyl-4-pyrimidinol as shown in Eq. 1.



(Eq. 1)

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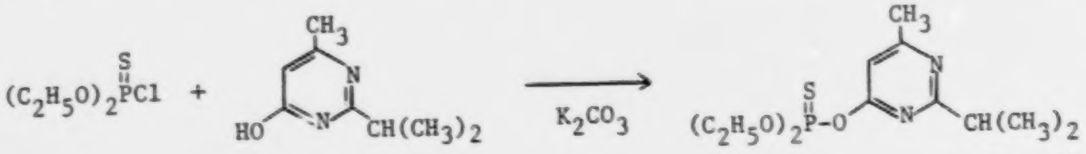
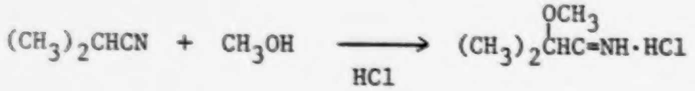


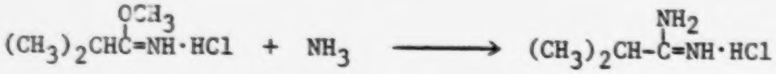
(Eq. 1)

The precursor 2-isopropyl-6-methyl-4-pyrimidinol is synthesized in three steps shown by Eqs. 2 through 4. O,O-Diethyl phosphorochlorothioate, the other precursor for diazinon, is not synthesized at this location but is shipped to the production site. This accounts for the relatively low number of phosphorothioates in the wastewater streams.



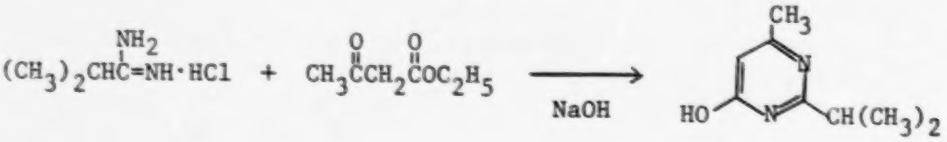
$$(CH_3)_2CHCN + CH_3OH \xrightarrow[HCl]{} (CH_3)_2CH\overset{OCH_3}{\overset{|}{C}}=NH\cdot HCl$$

(Eq. 2)



$$(CH_3)_2CH\overset{OCH_3}{\overset{|}{C}}=NH\cdot HCl + NH_3 \longrightarrow (CH_3)_2CH-\overset{NH_2}{\overset{|}{C}}=NH\cdot HCl$$

(Eq. 3)



(Eq. 4)

Compounds Identified--

All compounds identified by GC/MS in the three samples taken from this site are listed in Table 9. The compounds are listed in the following order: organophosphorus (1-4), miscellaneous (5-12) and volatiles (13-21). Organophosphorus esters that were detected in the derivatized fraction are listed as the underivatized compounds. Table 10 lists the methyl esters detected and the possible acid analogs of these esters.

Diazinon (1) was detected in the pretreatment sample as expected. It was not detected in the midtreatment sample which indicates the effect of acid hydrolysis on this compound. The decrease in concentration is more than can be accounted for by the factor of 5 dilution across the acid destruct pond. Diazoxon is an expected by-product of the synthesis and a possible degradation product. Its absence (< 0.006 mg/liter) in the pretreatment sample indicates the absence of O,O-diethyl phosphorochloridate impurity in the O,O-diethyl phosphorochlorothioate precursor. Diazoxon's absence in the midtreatment sample indicates that the acid catalyzed hyrolysis of the pyrimidinyl group is more rapid than oxidation of the thion group or that diazoxon also undergoes rapid acid catalyzed hydrolysis of the pyrimidinyl group. Neither compound was detected in the final effluent as was expected from their absence in the midtreatment sample.

TABLE 9. CONCENTRATION OF IDENTIFIED COMPOUNDS IN DIAZINON PRODUCTION PLANT WASTEWATER

No.	Compound identified	Concentration, mg/ℓ (ppm)		
		Pre-treatment	Mid-treatment	Post-treatment
1	Diazinon	2.0	< 0.006	< 0.006
2	O,O-Diethyl-S-hydrogen phosphorothioate[a]	DNQ[b]		
3	O,O-Diethyl-O-hydrogen phosphorothioate[a]	DNQ[b]		
4	O,O-Diethyl-O-hydrogen phosphate[a]	DNQ[b]		
5	2-Isopropyl-4-methoxy-6-methylpyrimidine	DNQ[b]	DNQ[b]	NA[c]
6	2-Isopropyl-4-ethoxy-6-methylpyrimidine	1.5	0.08	NA[c]
7	2-Isopropyl-6-methyl-4-pyrimidone	< 10	DNQ[b]	NA[c]
8	Ethyl isothiocyanate	DNQ[b]		NA[c]
9	N-Cyanodimethyl amine	DNQ[b]		NA[c]
10	Atrazine	< 10	0.04	NA[c]
11	Simazine	0.30		NA[c]
12	Propazine	0.060		NA[c]
13	Methanol	1,300	1,000	230
14	Ethanol	1,400	1,400	< 0.05
15	Acetone	300	170	16
16	Chloroform	140	25	3
17	1,1,1-Trichloroethane	300	< 0.05	< 0.05
18	Benzene	1.4	5	2
19	Toluene	3	< 0.05	< 0.05
20	Heptane	30	6	< 0.05
21	Ethyl isobutyrate	< 0.05	3	< 0.05

a/ Detected as O-methyl or S-methyl derivatives of indicated acid (see Table 10 for acid analogs).

b/ DNQ = Detected but not quantitated.

c/ NA = Not analyzed.

TABLE 10. ACID ANALOGS OF IDENTIFIED ESTERS IN DIAZINON PRODUCTION PLANT WASTEWATER

Compound identified	Acid analog
O,O-Diethyl-S-methyl phosphorothioate	O,O-Diethyl-S-hydrogen phosphorothioate
O,O-Diethyl-O-methyl phosphorothioate	O,O-Diethyl-O-hydrogen phosphorothioate
O,O-Diethyl-O-methyl phosphate	O,O-Diethyl-O-hydrogen phosphate

(2) O,O-Diethyl-S-hydrogen phosphorothioate and (3) O,O-diethyl-O-hydrogen phosphorothioate are both expected synthesis by-products. The hydrolysis of O,O-diethyl phosphorochlorothioate yields O,O-diethyl-O-hydrogen phosphorothioate. O,O-Diethyl-O-hydrogen phosphorothioate undergoes tautomerism to form O,O-diethyl-S-hydrogen phosphorothioate. The equilibrium favors the O-hydrogen isomer which is indicated by its higher concentration in the pretreatment sample. Neither compound was detected in the midtreatment or posttreatment samples, because of dilution or possible acid hydrolysis.

(4) O,O-Diethyl-O-hydrogen phosphate was detected in the pretreatment sample. The origin of this compound is the oxidation of either O,O-diethyl-S-hydrogen phosphorothioate or O,O-diethyl-O-hydrogen phosphorothioate. The absence of this compound in the midtreatment sample indicates acid hydrolysis of the O-ethyl ester groups.

(5) 2-Isopropyl-4-methoxy-6-methyl pyrimidine, (6) 2-isopropyl-4-ethoxy-6-methyl pyrimidine and (7) 2-isopropyl-6-methyl-4-pyrimidone are reaction by-products from the synthesis of 2-isopropyl-6-methyl-4-pyrimidinol (Eq. 4). These compounds are not affected by the acid destruct pond as indicated by their presence in the midtreatment sample at about the factor 5 dilution from the cyanuric chloride waste (Figure 3). Because of the addition of nonorganophosphorus wastewater between midtreatment and posttreatment, nonorganophosphorus compounds were not analyzed in the posttreatment sample.

(8) Ethyl isothiocyanate and (9) N-cyanodimethylamine were identified in the pretreatment sample. The exact origin of these compounds cannot be explained. They are structurally related to reaction intermediates for the preparation of the precursor 2-isopropyl-6-methyl-4-pyrimidinol (Eqs. 2 through 4).

(10) Atrazine, (11) Simazine and (12) Propazine were detected in the pretreatment sample. This was a surprising result because the diazinon wastewater system is segregated from the rest of the plant. Although the compounds are

produced at this site, they should not be present in the pretreatment sample. Atrazine was detected at reduced concentration in the midtreatment sample, indicating that it is somewhat stable to acid hydrolysis or also present in the cyanuric chloride wastewater.

(13) Methanol and (14) ethanol are used in the synthesis of diazinon (Eq. 2). The waste treatment system was not expected to be effective for these two alcohols. These compounds could also be added from other waste streams. The decrease in both compounds could result from dilution, evaporation, or degradation.

(15) Acetone, (16) chloroformm (18) benzene, (19) toluene, and (20) heptane are all likely process solvents for the production of diazinon and the other compounds at this facility. The specific solvents used for diazinon are unknown because they were classified as proprietary information. The waste treatment system is effective in decreasing the concentration of these low molecular weight nonpolar compounds. The likely removal process is evaporation during the aeration in the biological treatment as is indicated by the decrease in concentration between the midtreatment and posttreatment samples.

The presence of (17) 1,1,1-trichloroethane and (21) ethyl isobutyrate cannot be explained. Both compounds are removed before the final effluent.

Parathion Production

Wastewater Treatment System--

The wastewater treatment system is shown schematically in Figure 4.[4] The chlorinated acid wastewater from parathion production was sampled at location 2201 (pretreatment). Neutral wastewater from parathion production was sampled at location 2202 (midtreatment). The combined wastewater passes through aerobic biodegradation lagoons, clarifiers and finally at point 2203 (posttreatment) enters the city sewer system.

Twenty-four hour composite samples were taken at the pretreatment and midtreatment sampling locations. An 8-hr composite was made from grab samples taken at the posttreatment location. The pH's at the pretreatment, midtreatment and posttreatment samples were 0.7, 6.4, and 7.1, respectively. The flow at the pretreatment location is not measured. The flows at midtreatment and posttreatment are considered classified information by the production plant personnel.

It is difficult to determine the effect of the waste treatment process between the pretreatment and midtreatment samples because the volume of the pretreatment effluent was not measured and the water is diluted with nonacid wastes before the midtreatment sample location. The wastewater is not diluted beyond this point; the volumes of water leaving the midtreatment sampling location and the posttreatment location are monitored and are of nearly equal

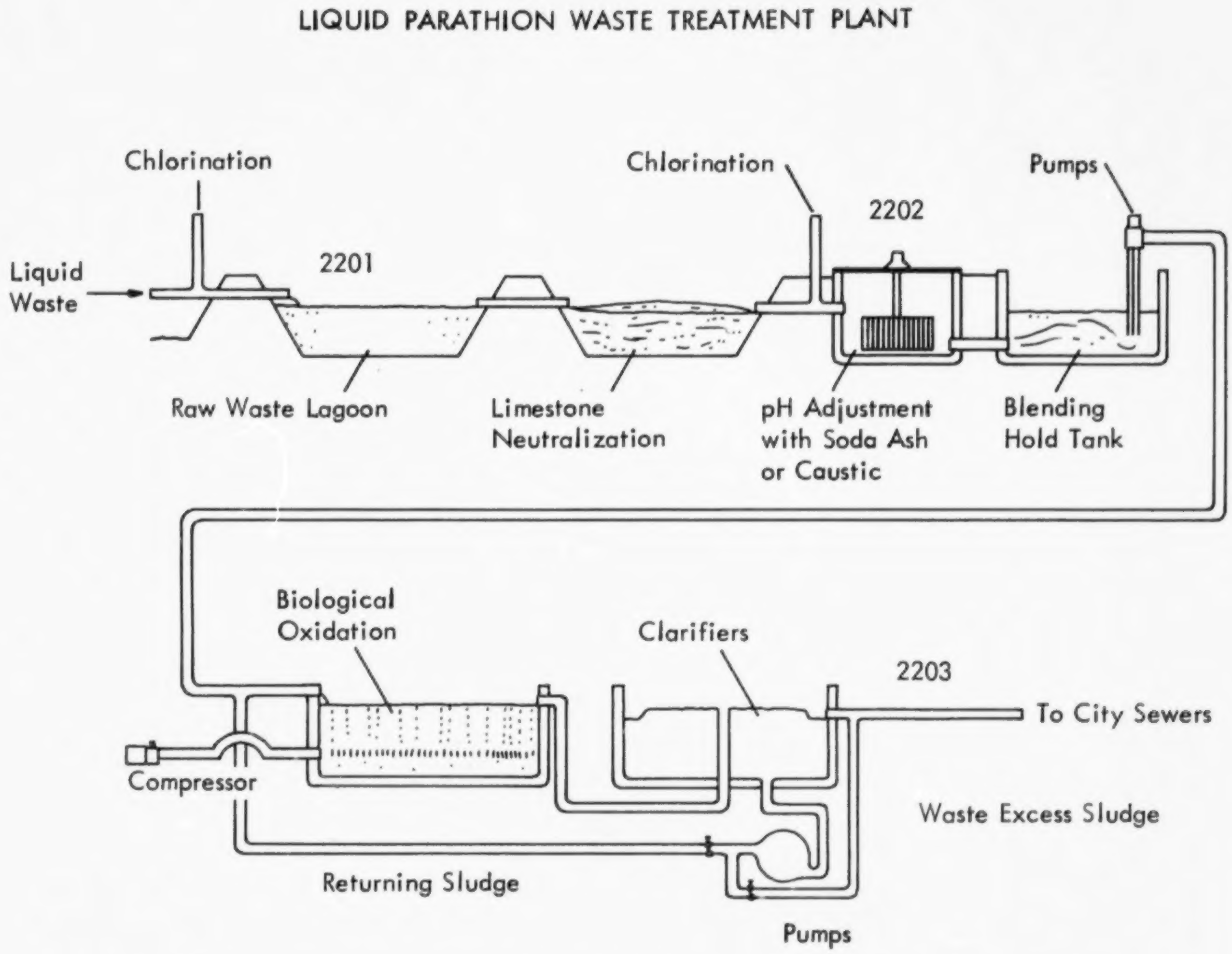
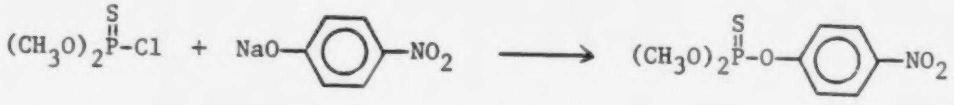

LIQUID PARATHION WASTE TREATMENT PLANT
Chlorination
Liquid Waste
2201
Raw Waste Lagoon
Limestone Neutralization
Chlorination
2202
pH Adjustment with Soda Ash or Caustic
Pumps
Blending Hold Tank
Biological Oxidation
Clarifiers
2203
To City Sewers
Compressor
Waste Excess Sludge
Returning Sludge
Pumps

Figure 4. Wastewater treatment sampling points for parathion production.

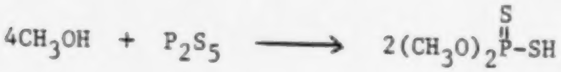
volume. Concentration differences between midtreatment and posttreatment can be attributed to the effects of the biotreatment process. This process can remove organophosphorus compounds by several mechanisms which include: aerobic biodegradation, air oxidation, adsorption onto the biomass, neutral hydrolysis, and vaporization.

Pesticide Synthesis Method--

The synthesis of methyl parathion is a simple condensation reaction between O,O-dimethyl phosphorochlorothioate and sodium *p*-nitrophenoxide, as shown in Eq. 5.

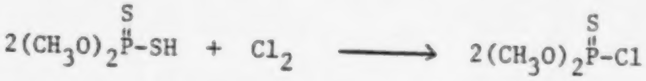

(Eq. 5)

Both precursors for methyl parathion synthesis are also made at this location. The preparation of O,O-dimethyl phosphorochlorothioate is a two-step process shown in Eqs. 6 and 7.



$$4CH_3OH + P_2S_5 \longrightarrow 2(CH_3O)_2\overset{S}{\overset{\|}{P}}\text{-}SH$$

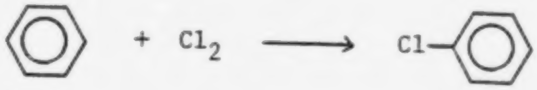
(Eq. 6)

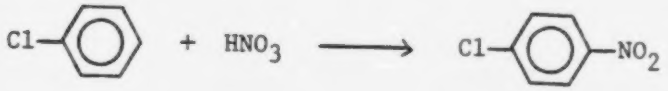


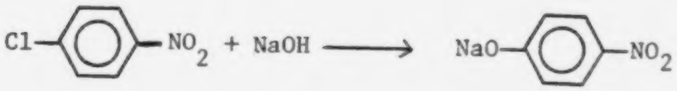
$$2(CH_3O)_2\overset{S}{\overset{\|}{P}}\text{-}SH + Cl_2 \longrightarrow 2(CH_3O)_2\overset{S}{\overset{\|}{P}}\text{-}Cl$$

(Eq. 7)

The preparation of sodium *p*-nitrophenoxide is a three-step process shown in Eqs. 8, 9, and 10.


(Eq. 8)


(Eq. 9)


(Eq. 10)

This production site makes ethyl parathion during part of the year and methyl parathion during the remainder of the year. The plant had switched from ethyl to methyl parathion just prior to our sampling. Because of this conversion, ethyl esters and methyl esters of the organophosphorus compounds were detected in the wastewater treatment system. The synthesis of ethyl parathion is identical to the synthesis of methyl except that ethanol is used in Eq. 6.

Compounds Identified--

All compounds identified by GC/MS in the three samples taken from the parathion production site are listed in Table 11. The compounds are grouped according to chemical class: organophosphorus (1-18), miscellaneous (19-25) and volatiles (26-34). Organophosphorus esters that were detected in the derivatized fractions are listed as the underivatized compounds. Table 12 lists the methyl esters detected and the possible acid analogs of these esters.

(1) O,O,O-Trimethyl phosphate (TMP) is produced from the reaction between O,O-dimethyl chlorophosphate and methanol. O,O-dimethyl chlorophosphate is a likely by-product formed during the generation of precursor O,O-dimethyl phosphorochlorothioate. TMP was detected only in the midtreatment sample. The biotreatment process is effective in removing the compound from the water.

(2) O,O,O-Trimethyl phosphorothioate is produced during the synthesis of O,O-dimethyl-S-hydrogen phosphorodithioate by the further addition of methanol and displacement of hydrogen sulfide. O,O,O-Trimethyl phosphorothioate was found at increasing concentration from pretreatment to posttreatment. This compound is either stable to acid hydrolysis or is added at midtreatment. The compound is resistant to the biotreatment process.

(3) O,O-Dimethyl-S-methyl phosphorodithioate is produced from the precursor O,O-dimethyl-S-hydrogen phosphorodithioate and methanol with the elimination of water. This compound was detected at nearly the same concentration in the pre- and midtreatment samples. It was detected in the final effluent but at one-tenth the concentration indicating that the compound is partially removed by the biotreatment process.

(4) O-Methyl-S,S-dimethyl phosphorodithioate is generated by the reaction of starting material, phosphorus pentasulfide, with O,O,O-trimethyl phosphate (compound 1 in Table 11). The highest concentration of the compound in the waste treatment stream was detected in the midtreatment samples. The concentration decreased to one-hundrth of its midtreatment concentration in the final effluent.

(5) O,O-Dimethyl-O-hydrogen phosphate, (6) O,O-dimethyl-O-hydrogen phosphorothioate, and (7) O,O-dimethyl-S-hydrogen phosphorothioate are expected hydrolysis products of Compounds 1 and 2. They decrease in concentration from midtreatment to posttreatment, which indicates the biotreatment process is effective in degrading partially hydrolyzed organophosphorus esters.

TABLE 11. CONCENTRATION OF IDENTIFIED COMPOUNDS IN PARATHION PRODUCTION PLANT WASTEWATER

No.	Compound identified	Concentration, mg/ℓ (ppm) Pretreatment	 Midtreatment	 Posttreatment
1	0,0,0-Trimethyl phosphate	< 0.002	0.08	< 0.002
2	0,0,0-Trimethyl phosphorothioate	2.7	3.9	4.4
3	0,0-Dimethyl-S-methyl phosphorodithioate	2.3	2.3	0.25
4	0-Methyl-S,S-dimethyl phosphorodithioate	0.02	0.3	0.002
5	0,0-Dimethyl-0-hydrogen phosphate[a]	0.07	2.7	< 0.006
6	0,0-Dimethyl-0-hydrogen phosphorothioate[a]	1.0	7.0	0.02
7	0,0-Dimethyl-S-hydrogen phosphorothioate[a]	3.5	2.3	0.03
8	0,0-Dimethyl-S-hydrogen phosphorodithioate[a]	4.1	3.1	< 0.008
9	0,0-Dimethyl phosphoramidothioate	< 0.002	2.1	2.8
10	0,0-Dimethyl-N-methyl phosphoramidothioate	< 0.002	< 0.002	0.16
11	Methyl parathion	2.0	3.2	< 0.004
12	Methyl paroxon	< 0.002	0.01	< 0.002
13	0-Methyl-0-hydrogen-0-(4-nitrophenol)phosphorothioate[a]	< 0.002	0.69	< 0.002
14	0,0,0-Triethyl phosphorothioate	< 0.002	0.03	< 0.002
15	0,0-Diethyl-S-methyl phosphorodithioate	0.80	0.76	0.16
16	0,0-Diethyl-S-ethyl phosphorodithioate	0.09	0.12	0.05
17	0,0-Diethyl-S-hydrogen phosphorodithioate[a]	2.7	< 0.004	< 0.008
18	Ethyl parathion	0.24	< 0.006	< 0.006
19	p-Methoxynitrobenzene	2.6	1.0	-
20	p-Nitrophenol	-	8.8	-
21	Chlorobenzene	0.3	0.3	0.76
22	p-Chlorophenol	3.1	-	-
23	p-Chloronitrobenzene	0.28	0.42	-
24	p-Chloroaniline	0.64	1.7	2.3
25	Hexachlorobenzene	-	-	~ 0.1
26	Acetone	250	370	0.9
27	Chloroform	0.02	0.02	-
28	Benzene	0.07	0.03	0.005
29	Dimethyl disulfide	0.45	0.60	-
30	Toluene	0.10	0.053	0.009
31	p-Xylene	0.08	0.004	-
32	m-Xylene	0.015	0.004	-
33	Methanol	98	29	8
34	Cyclohexane	-	-	0.07

[a] Detected as O-methyl or S-methyl derivative of indicated acid (see Table 12 for other possible compounds).

TABLE 12. ACID ANALOGS OF IDENTIFIED ESTERS IN PARATHION PRODUCTION PLANT WASTEWATER

Compound identified	Acid analog
0,0,0-Trimethyl phosphate	0,0-Dimethyl-0-hydrogen phosphate[a]
	0-Methyl-0,0-dihydrogen phosphate
0,0,0-Trimethyl phosphorothioate	0,0-Dimethyl-0-hydrogen phosphorothioate[a]
	0-Methyl-0,0-dihydrogen phosphorothioate
0,0-Dimethyl-S-methyl phosphorothioate	0,0-Dimethyl-S-hydrogen phosphorothioate[a]
	O-Methyl-S-methyl-O-hydrogen phosphorothioate
	S-Methyl-0,0-dihydrogen phosphorothioate
	O-Methyl-O-hydrogen-S-hydrogen phosphorothioate
0,0-Dimethyl-S-methyl phosphorodithioate	0,0-Dimethyl-S-hydrogen phosphorodithioate[a]
	O-Methyl-S-methyl-O-hydrogen phosphorodithioate
	0,0-Dihydrogen-S-methyl phosphorodithioate
	O-Methyl-O-hydrogen-S-hydrogen phosphorodithioate
0,0-Dimethyl-0-(4-nitrophenyl) phosphorothioate	O-Methyl-O-hydrogen-O-(4-nitrophenyl)phosphorothioate
	0,0-Dihydrogen-O-(4-nitrophenyl)phosphorothioate
0,0-Diethyl-S-methyl phosphorodithioate	0,0-Diethyl-S-hydrogen phosphorodithioate[a]

---

[a] The acid analog which is listed in Table 11; the true identity could be any of the listed analogs.

(8) O,O-Dimethyl-S-hydrogen phosphorodithioate is a precursor in the production of methyl parathion. It is formed from the reaction of methanol and phosphorus pentasulfide. The high concentration in pre- and midtreatment indicates that it does not undergo acid hydrolysis or that it is contained in the wastewater stream entering at the midtreatment location. The absence of O,O-dimethyl-S-hydrogen phosphorodithioate in the final effluent indicates efficient removal by the biotreatment process.

(9) O,O-Dimethyl phosphoramidothioate is an unexpected material to be found in methyl parathion wastewater. Its formation is possible by the addition of ammonium hydroxide to O,O-dimethyl-S-hydrogen phosphorodithioate or O,O-dimethyl chlorophosphorothioate. The source of ammonium hydroxide in the wastewater is unknown. O,O-Dimethyl phosphoramidothioate concentration is not significantly affected by the waste treatment as evidenced by the negligible change in concentration from mid- to posttreatment. A related compound, (10) O,O-dimethyl-N-methyl phosphoramidothiate was detected in the final effluent sample. It appears that the biological treatment results in some methylation of the amido group during treatment.

(11) Methyl parathion was detected in the acid waste pretreatment and in the midtreatment samples at similar concentrations. This indicates that either it does not undergo significant hydrolysis or the additional wastewater entering at this location contains methyl parathion. The final biotreatment process is very effective in removing methyl parathion from the water.

(12) Methyl paraoxon was detected in the midtreatment sample. Methyl parathion from the pretreatment sample could be oxidized to methyl paraoxon in the acid or limestone lagoons. The methyl paraoxon could also be introduced in the nonacid wastewater. Methyl paraoxon was not detected in the final effluent, indicating effective treatment.

(13) O-Methyl-O-hydrogen-O-(4-nitrophenyl) phosphorothioate is produced by the hydrolysis of a methoxy group from methyl parathion. This compound was only detected in the midtreatment sample, indicating that hydrolysis of methyl parathion occurs prior to or at this location. The absence of this compound in the final effluent indicates that additional degradation occurs in the biotreatment process.

(14) O,O,O-Triethyl phosphorothioate, (15) O,O-diethyl-S-methyl phosphorodithioate, (16) O,O-diethyl-S-ethyl phosphorodithioate, and (17) O,O-diethyl-S-hydrogen phosphorodithioate are ethyl analogs of Compounds 2, 3, and 8 from Table 11. The presence of these ethyl compounds is probably due to carryover in the acid waste holding pond from ethyl parathion production. The formation of these compounds can occur in the same manner described for the methyl analogs. The waste treatment has the same effect on their concentrations as that described for the methyl analogs.

(18) Ethyl parathion was detected in the acid waste holding pond but at no other location. The presence of ethyl parathion again indicates carryover from ethyl parathion production and some resistance of ethyl parathion to acid hydrolysis.

(19) *p*-Methoxynitrobenzene is produced from the reaction between *p*-nitrochlorobenzene and methanol or from the reaction of O,O,O-trimethyl phosphorothioate with sodium *p*-nitrophenoxide. The *p*-nitrochlorobenzene and sodium *p*-nitrophenoxide are precursors for the manufacture of methyl parathion. The O,O,O-trimethyl phosphorothioate is an identified impurity (3) detected in these samples at parts per million levels. *p*-Methoxynitrobenzene is eliminated during the waste treatment. *p*-Methoxyaniline, a primary biodegradation product, was not detected in the final effluent. This indicates that more extensive degradation is occurring.

(20) *p*-Nitrophenol can be formed from the hydrolysis of parathion or from the reaction between water and sodium *p*-nitrophenoxide. The most likely source is hydrolysis of the precursor sodium *p*-nitrophenoxide.

(21) Chlorobenzene is an intermediate product in the production of parathion. It is produced by the chlorination of benzene. The concentration of this compound was slightly increased by the waste treatment process. This could occur because of the chlorination of the wastewater, or the biodegradation of *p*-nitrochlorobenzene to remove the nitro but not the chloro group.

(22) *p*-Chlorophenol could be generated during methyl parathion synthesis if during chlorination of benzene some dichlorobenzene were formed. The dichlorobenzene would react with sodium hydroxide to generate *p*-chlorophenol. It is only detected in the acid waste stream (pretreatment sample). This is a surprising result because *p*-chlorophenol is expected to be relatively stable and would be expected at the other two sampling locations.

(23) *p*-Chloronitrobenzene is an intermediate product in the synthesis of parathion. It is produced by the nitration of chlorobenzene. The waste treatment process is effecient in removing this compound. The probable degradation product is (24) *p*-chloroaniline which appears at increasing concentration across the waste treatment system.

The presence of (25) hexachlorobenzene in the posttreatment sample cannot be easily explained. One possible source is the chlorination of benzene during the synthesis of sodium *p*-nitrophenoxide. However, if this were the case, hexachlorobenzene would be expected in the pre- and midtreatment samples.

(26) Acetone, (28) benzene, (31) *p*-xylene (32) *m*-xylene, and (33) methanol are expected solvents or starting materials used during the manufacture of parathion. They are found in highest concentration in the pretreatment

sample and decrease through the waste treatment system. The aeration basins are most efficient in removal of these compounds. The removal is likely to occur by vaporization during the aeration process.

The presence of (27) chloroform can result from chlorination of the wastewater. The chloroform concentration increased slightly with storage time, which indicates the possibility of sample contamination above the amount observed for the initial GC screen.

(29) Dimethyl disulfide is generated when methyl sulfide dimerizes in the presence of oxygen. The methyl sulfide is produced from hydrolysis of O,O-dimethyl-S-methyl phosphorodithioate. It is efficiently removed during the final treatment process.

The source of (30) toluene and (34) cyclohexane is not obvious. Toluene is a possible contaminate from Chromosorb 101 which is used as a GC column for VOA, but toluene did not elute during blank program runs.

Disulfoton and Azinphos-Methyl Production

Wastewater Treatment System--

The wastewater treatment system is shown schematically in Figure 5. This system treats disulfoton and azinphos-methyl manufacturing wastewater and waters from nonorganophosphorus (nitrogen-containing) agricultural chemical production. The wastewater treatment system consists of: solvent removal; gross pH adjustment; polymer reaction tank of unspecified function; an equalization tank which has a 3-day hold to adjust for variations in flow and concentration fluctuation; dilution to 60% with well water as the wastes leave the equalization tank; a splitter tank which directs wastewater to either one or both biotrains; biotrains which are aerobic liquor mass digestors; and a final clarifier before discharge.

The production site personnel would not permit sampling of the raw production wastewater. A midtreatment sample was taken from the site composite sampler after the splitter tank (2302 on Figure 5). This sample was at pH 7.6 and the average flow rate during the sampling period was 1,430 gal/min. The posttreatment sample was taken from the site's composite sampler after the final clarifier (2303 on Figure 5). This sample was at pH 7.3 and the average flow rate during the sampling period was 1,260 gal/min.

The wastewater treatment system at the site is designed to remove organic compounds by the following mechanism: solvent stripping; adsorption onto sludge and polymer; neutral hydrolysis, aerobic biodegradation, oxidation, and adsorption to secondary sludge. Because a pretreatment sample could not be taken, an overall evaluation of the treatment system could not be made. Analyses of the midtreatment and posttreatment samples allow an evaluation of the aerobic biodegradation and secondary clarifier.

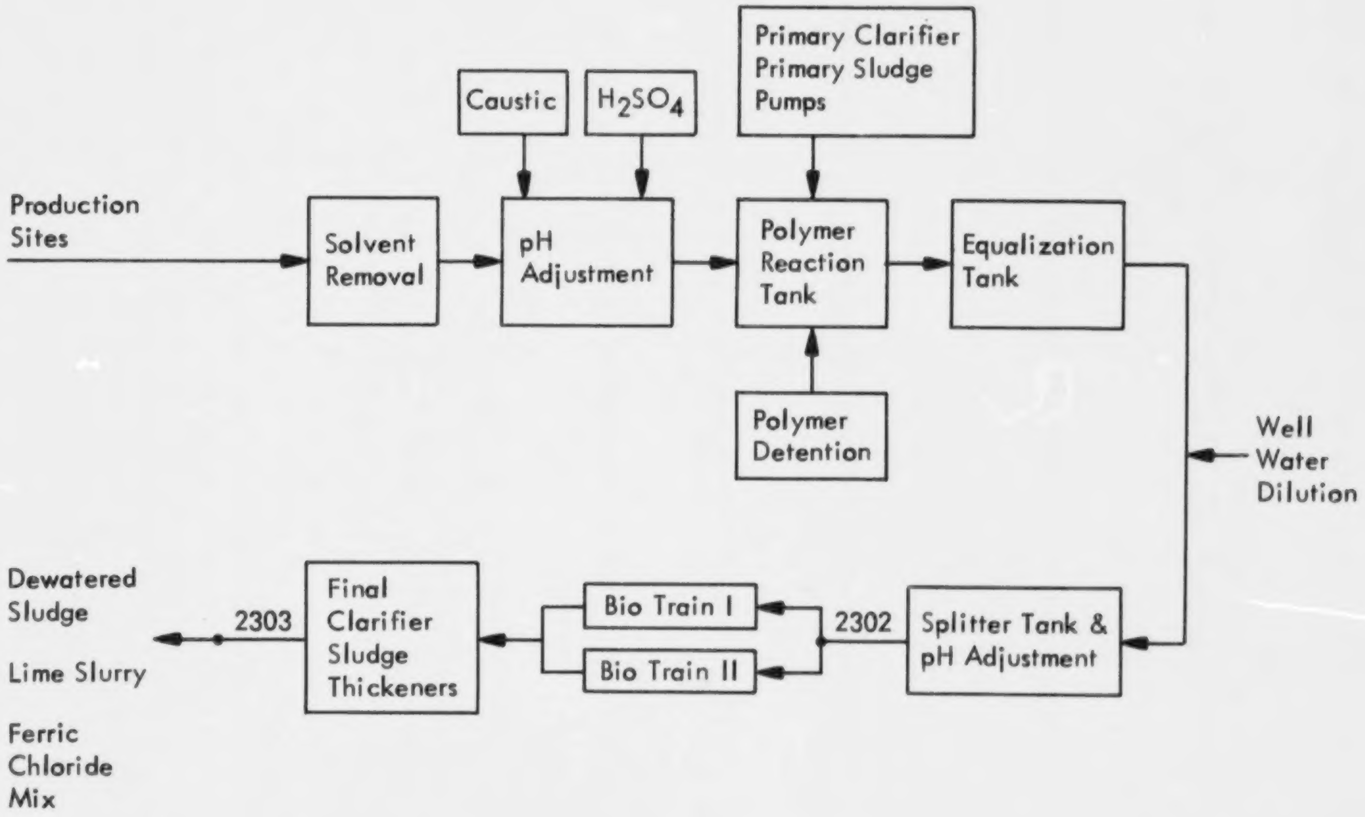
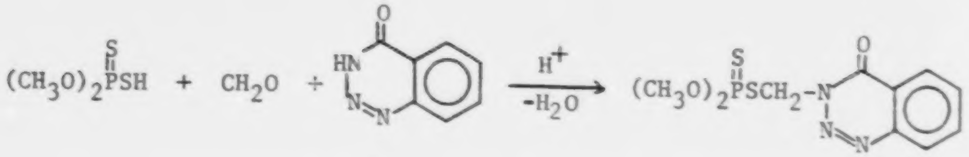

Production Sites
Solvent Removal
Caustic
H_2SO_4
pH Adjustment
Primary Clarifier Primary Sludge Pumps
Polymer Reaction Tank
Polymer Detention
Equalization Tank
Well Water Dilution
Splitter Tank & pH Adjustment
2302
Bio Train I
Bio Train II
Final Clarifier Sludge Thickeners
2303
Dewatered Sludge
Lime Slurry
Ferric Chloride Mix

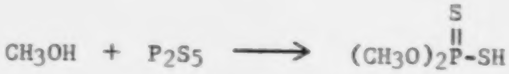
Figure 5. Wastewater treatment sampling points for disulfoton and azinphos-methyl production.

Pesticide Synthesis Methods--

Azinphos-methyl is prepared in a one-step synthesis from benzazimide, formaldehyde, and O,O-dimethyl phosphorodithioic acid as shown in Eq. 11.

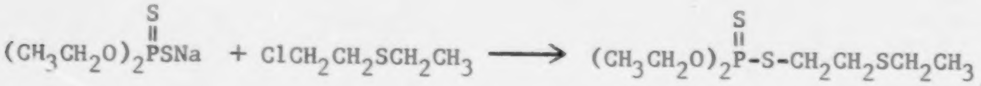

(Eq. 11)

O,O-Dimethyl phosphorodithioic acid is prepared by the following synthesis (Eq. 12).



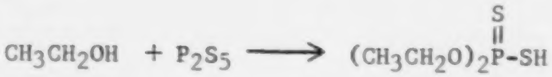
$$CH_3OH + P_2S_5 \longrightarrow (CH_3O)_2\overset{S}{\overset{\|}{P}}\text{-}SH \qquad \text{(Eq. 12)}$$

Disulfoton is prepared from sodium O,O-diethyl phosphorodithioic acid and 2-chlorodiethyl sulfide as shown in Eq. 13.



$$(CH_3CH_2O)_2\overset{S}{\overset{\|}{P}}SNa + ClCH_2CH_2SCH_2CH_3 \longrightarrow (CH_3CH_2O)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}CH_2CH_2SCH_2CH_3 \qquad \text{(Eq. 13)}$$

O,O-Diethyl phosphorodithioic acid is prepared by the following synthesis (Eq. 14).



$$CH_3CH_2OH + P_2S_5 \longrightarrow (CH_3CH_2O)_2\overset{S}{\overset{\|}{P}}\text{-}SH \qquad \text{(Eq. 14)}$$

Ethyl (Eq. 13) and methyl (Eq. 11) phosphorodithioates are used as precursors in the synthesis of these pesticides and both compounds are expected in wastewater samples.

Compounds Identified--

All compounds identified by GC/MS in the two samples taken from this site are listed in Table 13. The compounds are grouped into organophosphorus (1-9), miscellaneous (10-17), and volatile (18-27) classes. Organophosphorus esters that were detected in the derivatized fractions are listed as the underivatized compounds, i.e., as O-hydrogen rather than O-methyl. Table 14 lists the methyl esters detected and the possible acid analogs. Some of the alkyl esters were detected in the derivatized and underivatized fractions. These esters are not identified as acids unless the concentration of a given compound was greater for the derivatized fraction than for the underivatized fraction.

TABLE 13. CONCENTRATIONS OF IDENTIFIED COMPOUNDS IN AZINPHOS-METHYL AND DISULFOTON PRODUCTION PLANT WASTEWATER

No.	Compound identified	Concentration, mg/ℓ (ppm) Midtreatment	 Posttreatment
1	O,O,O-Triethyl phosphorothioate	< 0.02	0.5
2	O,O-Dimethyl-S-methyl phosphorodithioate	5	0.2
3	O,O-Diethyl-S-methyl phosphorodithioate	3	0.3
4	O-Methyl-S,S-dimethyl phosphorodithioate	6	< 0.02
5	O,O-Dimethyl-S-hydrogen phosphorodithioate[a]	21	< 0.02
6	O,O-Dimethyl-O-hydrogen phosphorothioate[a]	25	40
7	O,O-Diethyl-S-hydrogen phosphorodithioate[a]	6	4
8	O,O-Diethyl-O-hydrogen phosphorothioate[a]	< 0.02	6
9	S,S-Dimethyl hydrogen phosphite	< 0.02	0.08
10	4,4-Dimethyl-2-penten-2-ol	2	0.1
11	Alpha terpineol[b]	0.3	0.03
12	Terpineol[b]	0.1	< 0.02
13	6-Cyclohexylhexan-1-ol[b]	< 0.02	0.06
14	Secondary butyl iodide[b]	< 0.02	0.3
15	Methyl tridecyl octonoate[b]	0.09	0.03
16	2,2-Dimethyl propanoic acid[b]	< 0.02	0.08
17	p-Chlorobenzamide	0.01	< 0.02
18	Methanol	0.1	0.1
19	Ethanol	0.3	0.2
20	Acetone	0.5	0.1
21	Methylene chloride	0.6	0.5
22	1,2-Dichloroethylene	0.4	0.4
23	Chloroform	1.5	1.5
24	1,2-Dichloroethane	6	6
25	Benzene	0.04	0.06
26	Pinacolone	24[c]	10[c]
27	1,1,2,2-Tetrachloroethane	0.02	0.02

---

[a] Methyl analogs detected. See Table 14 for other possible acids.

[b] The identification is based on a similarity index match or on the *Eight Peak Index of Mass Spectra*, 1st ed., Mass Spectrometry Data Center, Aldermastun, Reading, U.K. (1970), and not on a match with a total reference spectrum. The identification is unconfirmed and should be considered tentative.

[c] Estimated concentration based on benzene response.

TABLE 14. ACID ANALOGS OF IDENTIFIED ESTERS IN AZINPHOS-METHYL AND DISULFOTON PRODUCTION PLANT WASTEWATER

Compound identified	Acid analog
0,0-Dimethyl-S-methyl phosphorodithioate	0,0-Dimethyl-S-hydrogen phosphorodithioate[a] 0-Methyl-S-methyl-0-hydrogen phosphorodithioate 0,0-Dihydrogen-S-methyl phosphorodithioate 0-Methyl-0-hydrogen-S-hydrogen phosphorodithioate
0,0,0-Trimethyl phosphorothioate	0,0-Dimethyl-0-hydrogen phosphorothioate[a] 0-Methyl-0,0-dihydrogen phosphorothioate
0,0-Diethyl-S-methyl phosphorodithioate	0,0-Diethyl-S-hydrogen phosphorodithioate[a]
0,0-Diethyl-0-methyl phosphorothioate	0,0-Diethyl-0-hydrogen phosphorothioate[a]

[a] The acid analog which is listed in Table 13; the true identity could be any of the listed analogs.

The effectiveness of the entire wastewater treatment system cannot be determined because an untreated sample could not be obtained. However, comparison of the compound concentrations at two sampling points (midtreatment and posttreatment) allows an evaluation of the biotrain and clarifier on the removal of organic compounds. The water volumes at the two sample locations are nearly the same, allowing direct comparison of solution concentrations. The biotrain and clarifier can remove organic compounds by several mechanisms, which include: aerobic biodegradation; chemical oxidation; adsorption on the biomass; neutral hydrolysis; and vaporization from the clarifier. The exact mechanism of removal cannot be determined, but neutral hydrolysis of organophosphorus compounds and vaporization of the high boiling compounds are not likely removal mechanisms. The possible source of each compound and the efficiency of the biotreatment process for removal of each compound are discussed below.

Neither azinphos-methyl nor disulfoton were identified in either sample. However, the analytical methodology for these compounds resulted in rather high detection limits. Azinphos-methyl was not eluted from either gas chromatographic column in a reasonable time; therefore the detection limit for this compound was established by TLC, i.e., approximately 0.25 mg/liter. The recovery of disulfoton was not consistent in the sample concentration step resulting in a detection limit of 0.050 mg/liter.

Known precursors account for all organophosphorus compounds (except the dimethyl phosphite) detected in the two samples. O,O-Dimethyl-S-hydrogen phosphorodithioate is a precursor in azinphos-methyl production. Solvolysis of this compound by methanol accounts for the methyl substituted compounds. O,O-Diethyl-S-hydrogen phosphorodithioate is the precursor in disulfoton production. Solvolysis of this compound by ethanol accounts for the ethyl substituted compounds.

(1) O,O,O-Triethyl phosphorothioate is produced during the synthesis of O,O-diethyl-S-hydrogen phosphorodithioate by the further addition of ethanol and displacement of hydrogen sulfide. The presence of this compound only in the final effluent sample indicates that it is formed during biotreatment. The likely precursor is O,O-diethyl-S-hydrogen phosphorodithioate, which was present in the posttreatment sample.

(2) O,O-Dimethyl-S-methyl phosphorodithioate is produced from the precursor O,O-dimethyl-S-hydrogen phosphorodithioate and methanol with the elimination of water. The concentration of this compound was decreased by the biotreatment process.

(3) O,O-Diethyl-S-methyl phosphorodithioate is produced from the precursor O,O-diethyl-S-hydrogen phosphorodithioate and methanol with the elimination of a water molecule. The concentration of this compound decreased by a factor of 10 through the biotreatment process. The likely degradation

product is O,O-diethyl-O-hydrogen phosphorothioate (8), which was detected in the posttreatment sample.

(4) O-Methyl-S,S-dimethyl phosphorodithioate is generated by the reaction of phosphorus pentasulfide (starting material) with O,O,O-trimethylphosphate. This compound was not detected in the final effluent, indicating efficient removal by the waste treatment system.

(5) O,O-Dimethyl-S-hydrogen phosphorodithioate and (6) O,O-dimethyl-O-hydrogen phosphorothioate are expected hydrolysis products of compound (2). Compound (5) decreases in concentration across the waste treatment system. Compound (6) increases from midtreatment to final effluent.

(7) O,O-Diethyl-S-hydrogen phosphorodithioate and (8) O,O-diethyl-O-hydrogen phosphorothioate are expected hydrolysis products of compounds (1) and (3). Compound (7) decreases in concentration and compound (8) increases in concentration across the biotreatment in the same manner as the methyl analogs (compounds (5) and (6)).

(9) S,S-Dimethyl hydrogen phosphite is not an expected degradation product or precursor for the synthesis of disulfoton or azinphos-methyl.

The identification of compounds (10) 4,4-Dimethyl-2-penten-2-ol, (11) alpha terpineol, (12) terpineol, (16) 2,2-dimethyl propanoic acid, and (26) pinacolone are tentative and based on a similarity index match or on the Eight Peak Index of Mass Spectra, 1st ed., Mass Spectrometry Data Center, Aldermastun, Reading, U.K. (1970), and not on a match with a total reference spectrum. These compounds are all structurally related compounds which could result from hydrolysis of the parent compound limonene. Limonene is used as a wetting and dispersing agent for water-insoluble compounds, and could be used during the formulation of pesticides. Limonene itself was not detected at the two sampling locations but alpha terpineol (11) was identified; it is the first hydrolysis product of limonene. Further hydrolysis of alpha terpineol (11) results in the formation of terpineol (12). Additional hydrolysis results in ring opening of the cyclohexane ring with minor rearrangements and would account for the presence of 4,4-dimethyl-2-penten-2-ol (10), pinacolone (26), and 2,2-dimethyl propanoic acid (16).

(17) p-Chlorobenzamide is not associated with the production of azinphos-methyl or disulfoton.

(13) 6-Cyclohexylhexan-1-ol, (14) secondary butyl iodide, and (15) methyl tridecyl octanoate were tentatively identified in the samples and not confirmed by matching with total reference spectra. Their presence in the wastewater treatment system cannot be attributed to the production of either pesticide.

(18) Methanol and (19) ethanol are expected starting materials for the synthesis of azinphosmethyl and disulfoton. Their concentrations do not decrease across the biotreatment because the wastewater system is enclosed from midtreatment to posttreatment sampling points.

(25) Benzene and (20) acetone are both expected process solvents used in the manufacture of organic compounds.

(21) Methylene chloride, (22) 1,2-dichloroethylene, (24) 1,2-dichloroethane, (23) chloroform, and (27) 1,1,2,2-tetrachloroethane are expected solvents and nonorganophosphorus intermediates used in pesticide manufacturing. These compounds could also result from the chlorination of wastewater that occurs during the synthesis step in which O,O-dimethyl-S-hydrogen phosphorodithioate and O,O-diethyl-S-hydrogen phosphorodithioate are converted to O,O-dimethyl chlorophosphorothioate and O,O-diethyl chlorophosphorothioate, respectively. The chlorination of methanol and ethanol could account for the chloromethanes and chloroethanes.

Fonofos, Phosmet and Bensulide Production

Wastewater Treatment System--

The wastewater treatment system is shown schematically in Figure 6. Rainwater runoff from the plant grounds is sent to the "Upset Sump." Other water from production activities may be periodically discharged into this "Upset Sump." This water is pH adjusted and the organic phase skimmed. The pretreatment sample (2401 on Figure 6) was taken at the inlet to the aeration pond. The water is aerated in an open, polyolefin-lined pond. There is some microbial growth in this pond but it is not designed for biotreatment. The pretreatment sample was a 24-hr composite sample. It had a pH of 10.5 and the volume for sampling period was 234,000 gal. The posttreatment sample (2402 on Figure 6) was a 24-hr composite sample. It was at pH 7.0. The flow was not metered at this location, but it is assumed to be the same as that at the pretreatment sample location because no additonal water is added and the aeration pond is maintained at constant volume. The pretreatment and posttreatment samples are not representative of the three pesticide production wastewaters which are injected into a deep well. The wastewater from the various production units are combined, and the pH is adjusted to 13 prior to injection into the deep well. The injection well sample (2403) was taken after the pH adjustment. A 24-hr composite sample was taken. The flow was measured at 66,000 gal. during the sampling period.

Production of phosmet, fonofos, thiocarbamates, thiophenol, and phosphorus trichloride occurred during the sampling period. The bensulide unit was in the process of coming back on-line during the sampling period. A power failure occurred during the sampling period for about 1 hr, which interrupted sampling and some poduction processes.

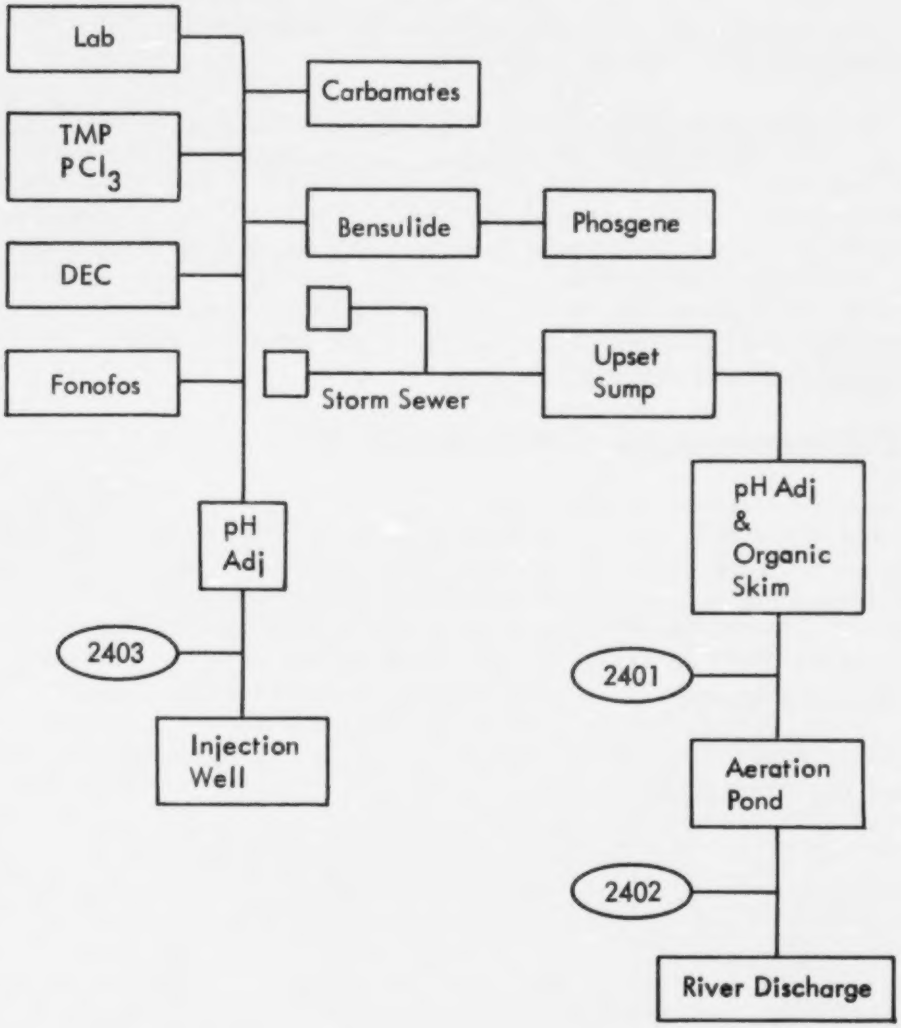

Lab
Carbamates
TMP
PCl3
Bensulide
Phosgene
DEC
Fonofos
Storm Sewer
Upset Sump
pH Adj
pH Adj & Organic Skim
2403
2401
Injection Well
Aeration Pond
2402
River Discharge

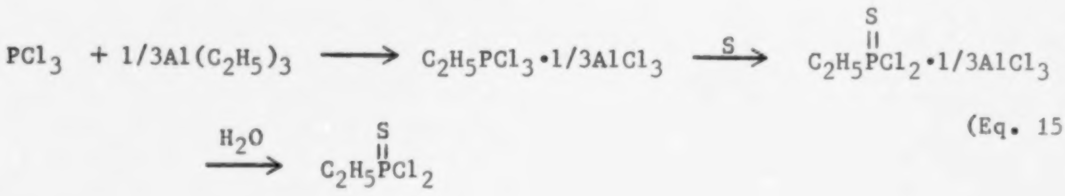
Figure 6. Wastewater treatment sampling points for fonofos, phosmet and bensulide production.

The water treatment across the aeration pond can remove compounds by any of the following methods: hydrolysis; air oxidation; adsorption onto suspended solids; and vaporization. The organophosphorus compounds would not be expected to be removed by vaporization and most undergo slow neutral hydrolysis.

The injection well is a waste disposal rather than waste treatment method. However, the sample is treated by pH adjustment prior to injection. The sample remained an average of 12 hr at pH 13 before neutralization of the composite sample. This exposed the organophosphorus compounds to base hydrolysis and any compounds detected in high concentration must be reasonably stable to this base hydrolysis.

Pesticide Synthesis Method--

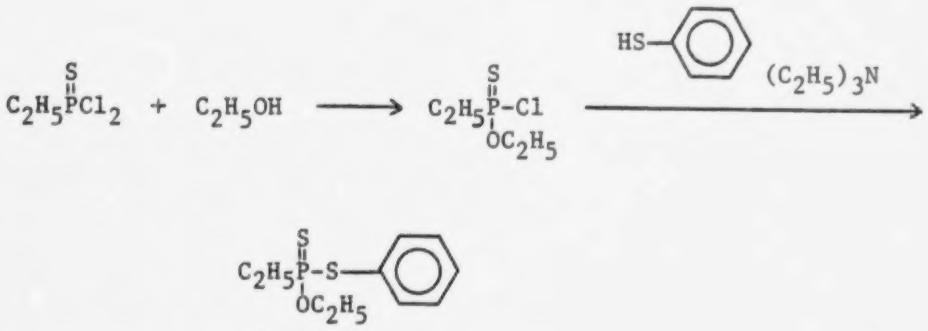
The origin of the identified compounds can be best discussed if the synthesis steps for the parent pesticides are known. The reactions for a possible synthesis of fonofos are shown below.[5/] The phosphorus-containing precursor is ethylphosphorothioic dichloride, which can be synthesized as shown in Eq. 15.



$$PCl_3 + 1/3Al(C_2H_5)_3 \longrightarrow C_2H_5PCl_3\cdot 1/3AlCl_3 \xrightarrow{S} C_2H_5\overset{S}{\overset{\|}{P}}Cl_2\cdot 1/3AlCl_3 \xrightarrow{H_2O} C_2H_5\overset{S}{\overset{\|}{P}}Cl_2$$

(Eq. 15)

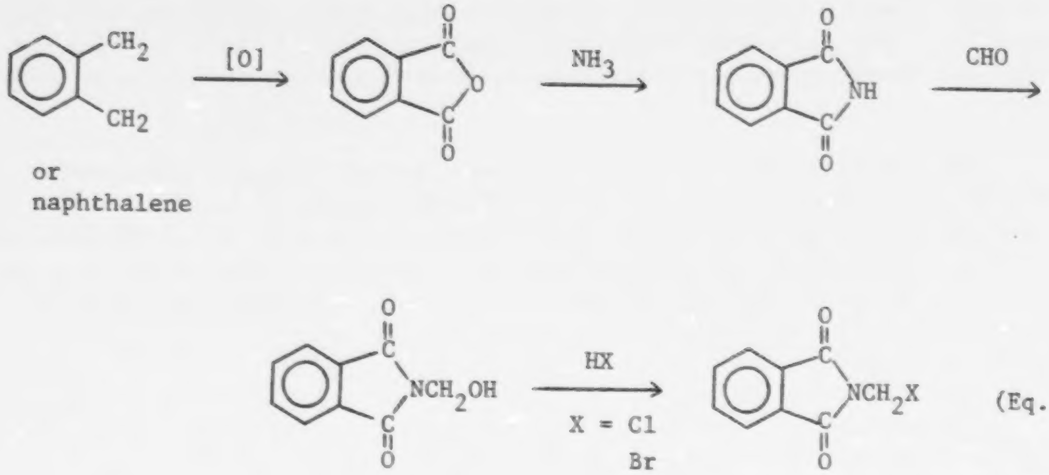
The synthesis of fonofos is given in Eq. 16.



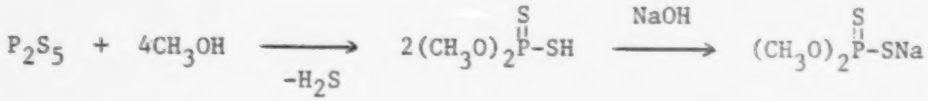
fonofos

(Eq. 16)

A possible synthesis for the two precursors of phosmet is given in Eqs. 17 and 18. The synthesis of phosmet is given in Eq. 19.

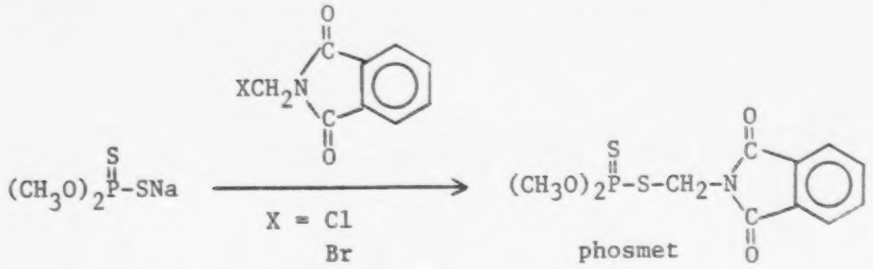

CH2
CH2
or
naphthalene
[O]
NH3
CHO
NCH2OH
HX
X = Cl
Br
NCH2X

(Eq. 17)



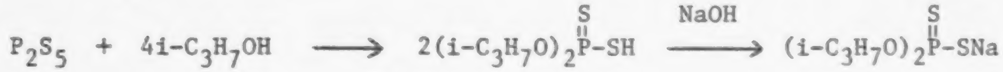
$$P_2S_5 + 4CH_3OH \xrightarrow[-H_2S]{} 2(CH_3O)_2\overset{S}{\overset{\|}{P}}\text{-}SH \xrightarrow{NaOH} (CH_3O)_2\overset{S}{\overset{\|}{P}}\text{-}SNa$$

(Eq. 18)


XCH2N
(CH3O)2P-SNa
S
X = Cl
Br
(CH3O)2P-S-CH2-N
phosmet

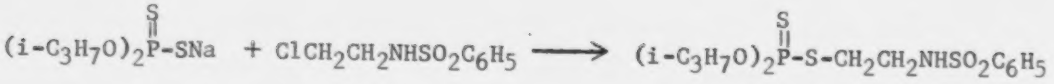
(Eq. 19)

The synthesis of bensulide is similar to that of phosmet because it is also a phosphorodithioate. The precursor preparation is shown in Eq. 20 and the final synthesis in Eq. 21.



$$P_2S_5 + 4i\text{-}C_3H_7OH \longrightarrow 2(i\text{-}C_3H_7O)_2\overset{S}{\overset{\|}{P}}\text{-}SH \xrightarrow{NaOH} (i\text{-}C_3H_7O)_2\overset{S}{\overset{\|}{P}}\text{-}SNa$$

(Eq. 20)



$$(i\text{-}C_3H_7O)_2\overset{S}{\overset{\|}{P}}\text{-SNa} + ClCH_2CH_2NHSO_2C_6H_5 \longrightarrow (i\text{-}C_3H_7O)_2\overset{S}{\overset{\|}{P}}\text{-S-}CH_2CH_2NHSO_2C_6H_5$$

bensulide (Eq. 21)

Trimethyl phosphite and triethyl phosphite are also produced at this site. The expected synthesis for these compounds is shown in Eq. 22.

$$PCl_3 + 3ROH + 3NR'_3 \longrightarrow (RO)_3P + 3R'_3NHCl \quad R = CH_3,\ C_2H_5 \qquad \text{(Eq. 22)}$$

Compounds Identified--

All compounds identified by GC/MS in the three samples taken from this site are listed in Table 15. The compounds are grouped into organophosphorus (1-10), thiocarbamates (11-15), miscellaneous (16-25), and volatiles 26-38). Organophosphorus esters that were detected in the derivatized fractions are listed as the underivatized compounds. Table 16 lists the methyl esters detected and the possible acid analogs.

The identification of organophosphorus compounds in samples from this location is complicated by the fact that methyl, ethyl, and propyl esters of phosphonates and phosphorothioates are possible. The potential number of compounds is very large and precludes prediction of all the possible compounds that might be present in the wastewater.

(1) O,O,O-Triethyl phosphate is produced from the oxidation of triethyl phosphite (Eq. 22). The concentration dropped significantly from pretreatment to posttreatment, indicating efficiency of the waste treatment system. It is surprising that this compound was not detected in the injection well sample.

(2) O,O-Dimethyl-O-ethyl phosphorothioate in the injection well sample may be due to the reaction of methanol and ethanol with phosphorus pentasulfide in the wastewater. The addition of ethanol to O,O-dimethyl phosphorodithioate (Eq. 18, phosmet precursor) with the elimination of hydrogen sulfide is another possible explanation for its presence.

(3) O,O-Diisopropyl-S-methyl phosphorodithioate is produced from the bensulide precursor O,O-diisopropyl-S-hydrogen phosphorodithioate (Eq. 20) and methanol with the elimination of a water molecule. This compound was detected in the injection well sample which indicates stability to base hydrolysis.

(4) O,O-Diethyl ethylphosphonothioate is produced from O-ethyl ethylphosphonochlorothioate (intermediate Eq. 16) by addition of ethanol and removal of hydrochloric acid. The waste treatment system is effective in the removal of this compound.

TABLE 15. CONCENTRATION OF IDENTIFIED COMPOUNDS IN FONOFOS, PHOSMET AND BENSULIDE WASTEWATER

No.	Compound identified	Concentration, mg/liter (ppm) Pre-treatment	Post-treatment	Injection well
1	O,O,O-Triethyl phosphate	0.75	< 0.002	< 0.002
2	O,O-Dimethyl-O-ethyl phosphorothioate	< 0.002	< 0.002	3.5
3	O,O-Diisopropyl-S-methyl phosphorodithioate	< 0.01	< 0.01	4
4	O,O-Diethyl ethylphosphonothioate	0.75	0.02	< 0.01
5	Exo-2-dimethyl phosphono-2-hydroxynorbornene	1	< 0.01	< 0.01
6	Fonofos	~ 0.001[a]	~ 0.001[a]	0.6
7	O,O-Diisopropyl-S-hydrogen phosphorodithioate[b]	< 0.01	< 0.01	50
8	O,O-Dimethyl-O-hydrogen phosphorothioate[b]	< 0.01	< 0.01	50
9	O-Ethyl-O-hydrogen ethylphosphonate[b]	< 0.01	< 0.01	12
10	O,S-Diisopropyl-O-hydrogen phosphorodithioate[b]	0.04	< 0.01	< 0.01
11	EPTC	1.1	0.02	80
12	Vernolate	0.2	< 0.05	58
13	Molinate	0.1	0.38	12
14	Pebulate	< 0.05	< 0.05	0.1
15	Cycloate	0.3	0.07	27
16	Diphenyl disulfide[c]	< 0.05	< 0.05	42
17	1-Thioldiethyl disulfide	< 0.05	< 0.05	4
18	1(Methyl mercapto)diethyl disulfide	< 0.05	< 0.05	120
19	Diethyl aniline[c]	< 0.05	< 0.05	0.1
20	Pyrrolizidine[c,d]	15	< 0.05	< 0.05
21	Methyl palmitate[c,d]	0.6	< 0.05	< 0.05
22	Methyl oleate[c,d]	0.3	< 0.05	< 0.05
23	Methyl N-tetradeconate[c,d]	0.1	< 0.05	< 0.05
24	Cyclohexanol[c]	< 0.05	< 0.05	4
25	Phenyl ethyl disulfide[c]	< 0.05	< 0.05	0.4
26	Ethanol	1	ND[e]	620
27	Propanol	ND[e]	ND[e]	6
28	Acetone-ethyl ether	18	17	ND[d]
29	Methylene chloride	13	11	ND[d]
30	1,2-Dichloroethylene	0.6	0.5	ND[d]
31	1,2-Dichloroethane	0.4	0.3	ND[d]
32	Chloroform	0.6	0.9	ND[d]
33	Benzene	6	3	4
34	Toluene	0.01	0.01	0.55
35	Dimethyl sulfide	ND[e]	ND[e]	0.08
36	Methyl ethyl sulfide	ND[e]	ND[e]	0.3
37	Diethyl disulfide	ND[e]	ND[e]	8
38	Phenyl acetate	ND[e]	ND[e]	0.03

a/ Concentration estimated from extracted ion current plots.

b/ Detected as methyl derivatives of the corresponding hydroxy or thio compounds.

c/ Concentration estimated from GC/MS response and calculated relative to diazinon standard.

d/ The identification is based on a similarity index match or on the Eight Peak Index of Mass Spectra, 1st ed., Mass Spectrometry Data Center, Aldermastun, Reading, U.K. (1970), and not on a match with a total reference spectrum. The identification is unconfirmed and should be considered tentative.

e/ Not detected; detection limit not established.

TABLE 16. ACID ANALOGS OF IDENTIFIED ESTERS IN FONOFOS, PHOSMET AND BENSULIDE WASTEWATER

Compound identified	Acid analog
0,0-Diisopropyl-S-methyl phosphorodithioate	0,0-Diisopropyl-S-hydrogen phosphorodithioate
0,0,0-Trimethyl phosphorothioate	0,0-Dimethyl-0-hydrogen phosphorothioate[a] 0-Methyl-0,0-dihydrogen phosphorothioate
0-Ethyl-0-methyl ethyl phosphonate	0-Ethyl-0-hydrogen ethylphosphonate
0,S-Diisopropyl-0-methyl phosphorodithioate	0,S-Diisopropyl-0-hydrogen phosphorodithioate

---

[a] The acid analog which is listed in Table 15; the true identity could be either of the listed analogs.

(5) Exo-2-dimethyl phosphono-2-hydroxy norbornene was identified tentatively from a low similarity index match only and is probably not present in the sample.

(6) Fonofos is one of the pesticides produced at this location. It was detected at low levels in the pretreatment and posttreatment samples. The concentration in the injection well sample was higher but below 1 ppm.

(7) O,O-Diisopropyl-S-hydrogen phosphorodithioate was found at high levels in the injection well sample. The compound is a precursor for the synthesis of bensulide (Eq. 20). It is also an expected base hydrolysis product of bensulide.

(8) O,O-Dimethyl-O-hydrogen phosphorothioate is an hydrolysis product of the phosmet precursor O,O-dimethyl-S-hydrogen phosphorodithioate (Eq. 18). It could also be formed from the hydrolysis of phosmet at the P-S bond. It was detected only in the injection well sample. This compound appears to be stable to base hydrolysis.

(9) O-Ethyl-O-hydrogen ethylphosphonate is an expected degradation product of the precursor O-ethyl ethylphosphonochlorothioate and a hydrolysis product of fonofos (Eq. 16).

(10) O,S-Diisopropyl-O-hydrogen phosphorodithioate could be produced from a rearrangement reaction of compound (7) and therefore a by-product of the precursor for bensulide. It does not appear to be stable to base hydrolysis because it is absent in the injection well sample. The waste treatment system is efficient in the removal of the compound.

(11) EPTC, (12) vernolate, (13) molinate, (14) pebulate, and (15) cycloate are all thiocarbamates produced at this location. Small amounts of EPTC, vernolate, molinate, and cycloate were detected in the pretreatment sample. EPTC, vernolate, molinate, and cycloate were detected at high concentration (12 to 80 ppm) in the injection well sample indicating stability to base hydrolysis (see Appendix A for structures).

(16) Diphenyl disulfide, (17) 1-thioldiethyl disulfide, (18) 1-(methyl mercapto)diethyl disulfide and (25) phenyl ethyl disulfide are sulfur-containing compounds associated with the manufacture of organophosphorus and thiocarbamate compounds. Thiophenol is synthesized at this site for use in the production of fonofos (Eq. 16). Oxidation of the phenol would produce diphenyl disulfide. 1-Thioldiethyl disulfide and 1-(methyl mercapto)diethyl disulfide may be formed from the various methyl and ethyl mercaptans that are base hydrolysis products in the injection well sample in the same manner as diphenyl disulfide .

(19) Diethyl aniline and (20) pyrrolizidine are nitrogen-containing compounds which may be by-products from the thiocarbamate synthesis. Pyrrolizidine identification was based on a similarity index match only and is considered to be tentative.

(21) Methyl palmitate, (22) methyl oleate, and (23) methyl N-tetradecanate are methyl esters of high molecular weight carboxylic acids that were tentatively identified. Their presence in the pretreatment sample cannot be explained.

(24) Cyclohexanol can be readily associated as a synthesis precursor. Cyclohexanol is an expected starting material for the production of cycloate.

(26) Ethanol and (27) iso-propanol are precursors for fonofos and bensulide production (Eqs. 16 and 19, respectively). Ethanol was detected in pretreatment and not posttreatment, indicating efficient removal.

(28) Acetone/ethyl ether, (29) methylene chloride, (32) chloroform, (33) benzene, and (34) toluene are all likely process solvents. All of these compounds are found at about the same concentration in the pretreatment and posttreatment samples, indicating inefficient removal.

(30) 1,2-Dichloroethylene and (31) 1,2-dichloroethane are both detected in the pretreatment and posttreatment samples. Their origin is not apparent. It is possible that they are formed during the reaction of phosphorus trichloride and triethyl aluminum if excess phosphorus trichloride is present. This is not confirmed because of the absence of either compound in the injection well sample.

(35) Dimethyl sulfide, (36) methyl ethyl sulfide and (37) diethyl disulfide are all expected by-products from the synthesis of organophosphorus and thiocarbamate compounds. The high concentration of diethyl disulfide, along with other disulfides, accounted for much of the strong unpleasant odor exhibited by the injection well sample.

(38) Phenyl acetate, which was detected in the injection well sample, is not a known process chemical.

The major constituents of the injection well sample were unidentified disulfide compounds of MW 218, which were similar to diphenyl disulfide . These compounds were not observed in the other two samples.

Bensulide would not chromatograph on either Carbowax or OV-1. A chromatographic system was not developed for this single compound. The GC/MS data for J fractions on OV-1 were analyzed for mass characteristic peaks but no bensulide was detected. Bensulide was tentatively identified in the pretreatment sample by TLC indicating a concentration above 20 ppm. It was not present in sufficient concentration to obtain IR spectra for further confirmation. Failure to detect bensulide in the injection well sample by TLC indicates the base hydrolysis is effective in decreasing its concentration below the 20 ppm level.

No phosmet standard was available at the time these samples were analyzed. It was not known prior to sampling that this facility was producing phosmet. It is not listed in Chemical Sources as a compound made at this location and there was no indication during the presite selection visit that this compound was being made.

Literature values[6/] suggest that phosmet would have a relative retention value of approximately 2.5 (diazinon = 1.0) on OV-1 under the chromatographic conditions used for these analyses and would have been detected if present. The GC/MS results for J fractions on OV-1 were checked for more characteristic peaks, but phosmet was not detected. Phosmet was not in MRI TLC data of standards; therefore, TLC confirmation of results was not possible.

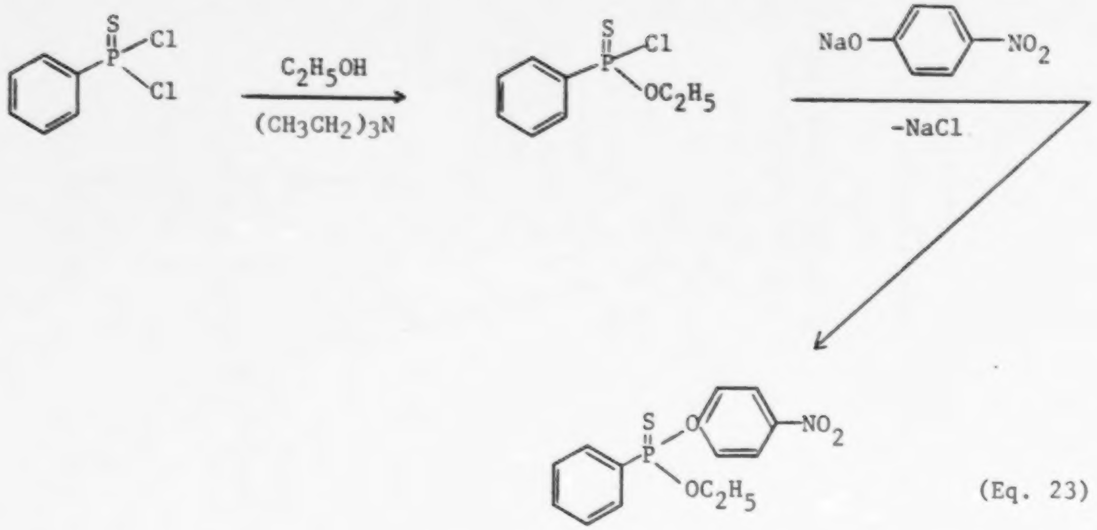
EPN Production

Wastewater Treatment System--

The EPN production site employs two different waste disposal systems that handle their chemical and process wash stream waste separately from the effluent consisting primarily of rain runoff, blowdown and washdown waters. Primary production waste is disposed of by off-site deep-well injection; samples were not taken of this material. The site discharges the runoff-washdown effluent into the Bio-San channel of an industrial area's central waste treatment plant that treats wastes from approximately 35 plants of various types. This system is shown schematically in Figure 7. It consists of: preaeration, activated sludge treatment with clarification and sludge recycle, chlorination, and final polishing where additional natural biological stabilization occurs. The pretreatment sample was taken of the EPN effluent just prior to discharge into Bio-San channel. There was no information to indicate waste processing prior to this discharge point. The posttreatment sample was taken following chlorination but prior to the final polishing stage.

Pesticide Synthesis Methods--

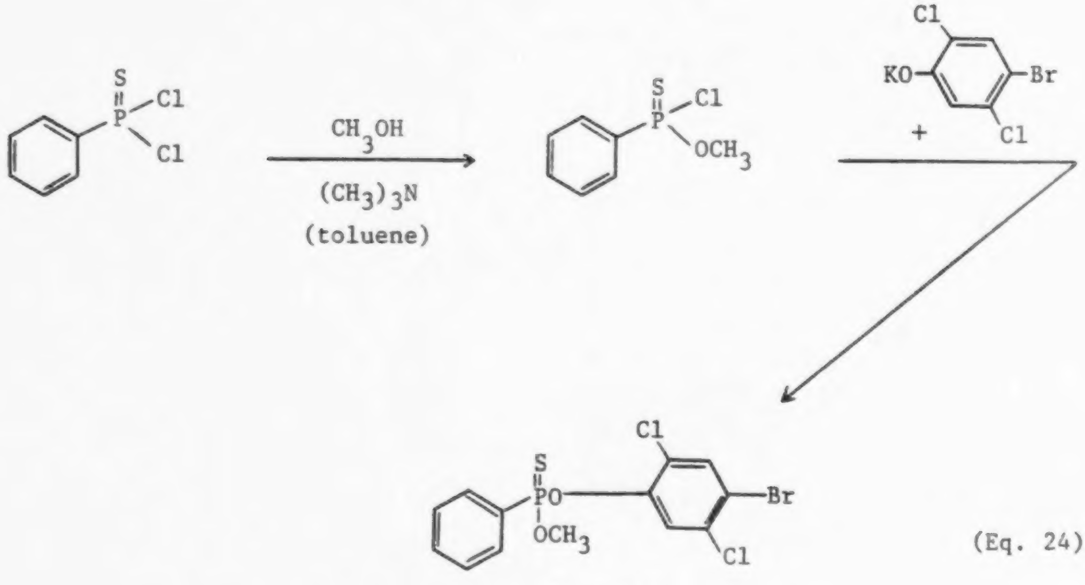
According to information provided by personnel from the production site EPN was being produced during the sampling period and leptophos, which also had been manufactured at this site, had not been in production for at least a year prior to sample collection. The synthesis methods for EPN and leptophos are outlined in Eqs. 23 and 24, respectively.



S
Cl
Cl
C2H5OH
(CH3CH2)3N
S
Cl
OC2H5
NaO
NO2
-NaCl
S
O
NO2
OC2H5

EPN

(Eq. 23)



S
Cl
Cl
CH3OH
(CH3)3N
(toluene)
S
Cl
OCH3
Cl
KO
Br
+
Cl
S
PO
OCH3
Cl
Br
Cl

leptophos

(Eq. 24)

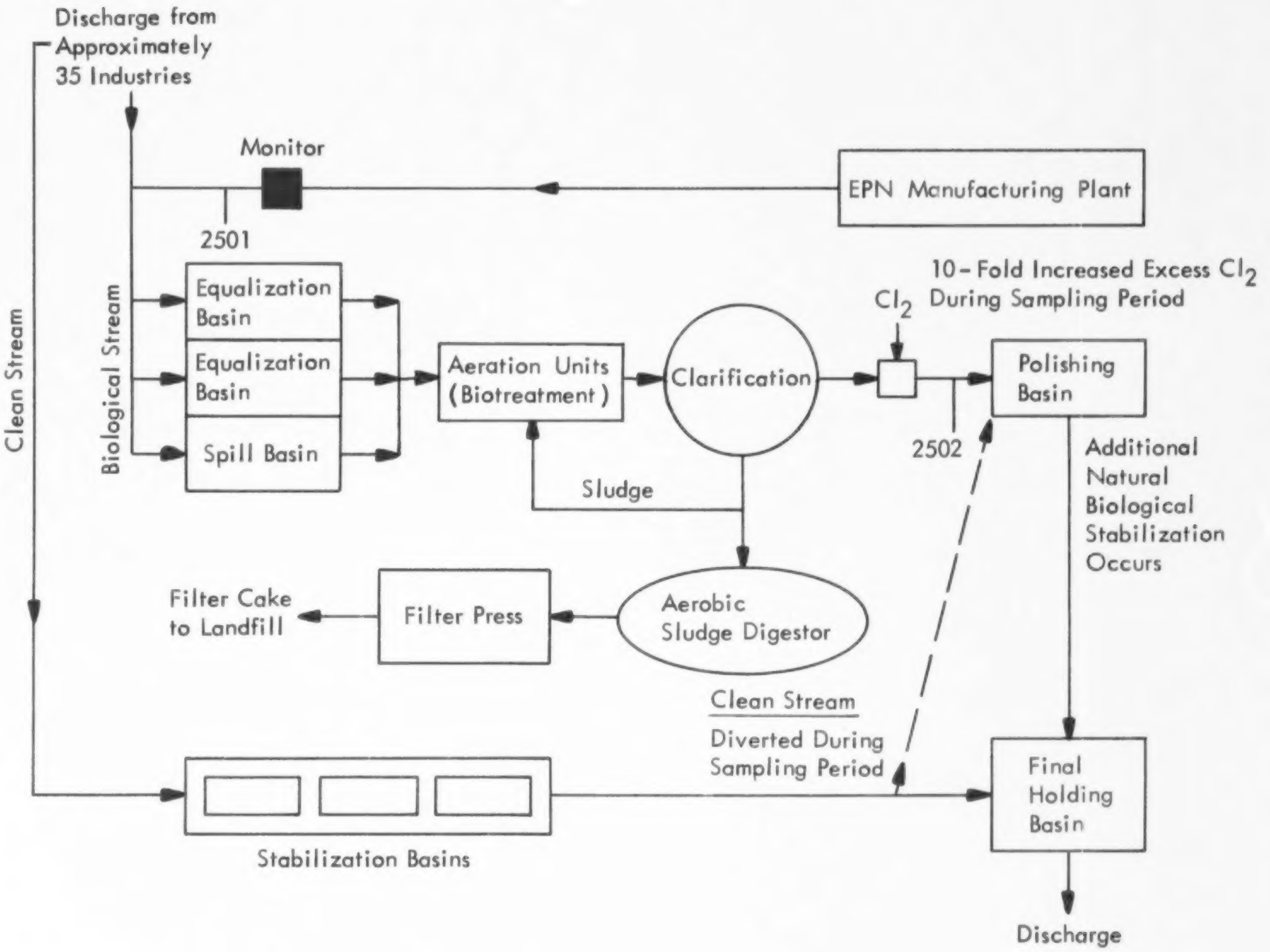

Discharge from
Approximately
35 Industries
Monitor
2501
EPN Manufacturing Plant
Clean Stream
Biological Stream
Equalization Basin
Equalization Basin
Spill Basin
Aeration Units (Biotreatment)
Clarification
Cl_2
10-Fold Increased Excess Cl_2 During Sampling Period
Polishing Basin
2502
Sludge
Additional Natural Biological Stabilization Occurs
Filter Cake to Landfill
Filter Press
Aerobic Sludge Digestor
Clean Stream
Diverted During Sampling Period
Final Holding Basin
Stabilization Basins
Discharge

Figure 7. Wastewater treatment sampling points for EPN production.

Compounds Identified--

All compounds identified by GC/MS in the two samples are listed in Table 17. Because of the additional wastewater stream from other industries that enter between the two sampling locations, only organophosphorus compounds were analyzed in the posttreatment sample. The compounds in Table 17 are grouped into organophosphorus (1-19), miscellaneous (20-27) and volatiles 28-39). Organophosphorus esters that were detected in the derivatized fractions are listed as the underivatizedcompounds. Table 18 lists the methyl esters detected and the possible acid analogs.

All the organophosphorus compounds, with the exception of O(chlorobromoaminophenyl) O-methyl phenylphosphonate, identified in the treated sample were also present in untreated effluent. In general, the reduction in their concentration across the waste treatment system is approximately equivalent to the dilution factor (1 to 250) across the system. A discussion of the identified compounds follows.

(2) O-Ethyl S-hydrogen phenylphosphonothioate could result from partial alkaline hydrolysis of O-(4-nitrophenyl) O-ethyl phenylphosphonothioate (EPN) in the pH 8.8 untreated effluent. Further hydrolysis would be retarded under the neutral conditions at the central waste treatment facility.

(4) O-Ethyl O-hydrogen phenylphosphonate is an expected hydrolysis product of the oxygen analog of EPN. Chemical oxidation of EPN is likely to occur during the production process. The stability of this compound in the neutral environment between sampling points is predictable as is the case with (2). The para nitrophenyl group is the preferred leaving group under nucleophilic attack.

(17), (18) O-(4-Nitrophenyl) O-ethyl chlorophenylphosphonothioate isomers may be reaction products of EPN with a strong halogenating agent such as NaOCl (formed from Cl_2 in the presence of base). The persistence of this compound might be explained by increased stability to alkaline hydrolysis induced by addition of a halogen to the ring attached directly to the phosphorus.

(13), (14) O-(Chloroaminophenyl) O-methyl phenylphosphonate isomers, (16) O-(chlorobromoaminophenyl) O-methyl phenylphosphonate, and (19) O-(chlorobromoaminophenyl) O-ethyl phenylphosphonate can more easily be associated with the production of leptophos than that of EPN. The aminophenyl moities might be intermediates in the Sandmeyer reaction for preparation of aryl halides. In this procedure, the amino group is diazotized and the diazonium salt group is replaced by a halogen. However, since the published[7/] industrial production synthesis uses potassium 4-bromo-2,5-dichlorophenolate as a starting material, the origin of compounds (13), (14), (16), and (19) is still in question.

TABLE 17. CONCENTRATIONS OF IDENTIFIED COMPOUNDS IN EPN PRODUCTION PLANT WASTEWATER[a]

No.	Compound identified	Concentration, mg/liter (ppm) Pre-treatment	 Post-treatment
1	O-Hydrogen S-ethyl phenylphosphonothioate[b]	1.4	ND[c]
2	O-Ethyl S-hydrogen phenylphosphonothioate[b]	0.94	0.008
3	O-Methyl-O-hydrogen phenylphosphonate[b]	≯ 1.4[d]	ND[c]
4	O-Ethyl O-hydrogen phenylphosphonate[b]	≯ 1.4[d]	0.04
5	O-Methyl S-hydrogen phenylphosphonothioate[b]	≯ 0.04[d]	ND[c]
6	O-Methyl S-ethyl phenylphosphonothioate	≯ 0.04[d]	ND[c]
7	O,O-Diethyl chlorophenylphosphonothioate	0.61	ND[c]
8	O,O-Diethyl phenylphosphonothioate	0.12	ND[c]
9	O,O-Dimethyl phenylphosphonothioate	0.04	ND[c]
10	O-Ethyl phenylphosphonochlorothioate	0.29	ND[c]
11	O,S-Diethyl phenylphosphonothioate	4.08	ND[c]
12	O,O-Diethyl phenylphosphonate	1.25	ND[c]
13	O-(Chloroaminophenyl) O-methyl phenylphosphonate	0.06	ND[c]
14	Isomer of 13	0.06	ND[c]
15	O-(4-Nitrophenyl) O-ethyl phenylphosphonothioate (EPN)	9.1[e] 21[f]	ND[c]
16	O-(Chlorobromoaminophenyl) O-methyl phenylphosphonate	ND[c]	0.007
17	O-(4-Nitrophenyl) O-ethyl chlorophenylphosphonothioate	0.29	0.002
18	Isomer of 17	0.13	
19	O-(Chlorobromoaminophenyl) O-ethyl phenylphosphonate	0.22	0.002
20	m-Dichlorobenzene	0.28[g] 0.008[h]	ND[c]
21	p-Dichlorobenzene	1.3[g] 0.013[h]	ND[c]
22	Trichlorobenzene	0.02	ND[c]
23	Biphenyl	2.08	ND[c]
24	Cresol homolog	0.01	ND[c]
25	2-Chlorobiphenyl	0.01	ND[c]
26	2,4-Dichlorophenol	0.01	ND[c]
27	Diisobutylphthalate	0.10	ND[c]
28	Ethanol	31	ND[c]
29	Diethyl ether	22	12
30	1,2-Dichloroethylene	0.3	0.2
31	1,2-Dichloroethane	0.3	0.44
32	Chloroform	0.8	0.6

(continued)

TABLE 17 (continued)

No.	Compound identified	Concentration, mg/liter (ppm) Pre-treatment	 Post-treatment
33	Benzene	7	5
34	Toluene	0.8	0.02
35	Chlorobenzene	0.02	ND[c]
36	Diethyl disulfide	0.04	ND[c]
37	Methylene chloride	ND[c]	6
38	m-Xylene[i]	ND[c]	0.01
39	p-Xylene[i]	ND[c]	0.01

---

a/ Not process wastewater; these samples were surface water runoff from the production area. Process wastewater is deep well injected off-site.

b/ Methyl ester detected (see Table 18 for other possible acids and the methyl esters).

c/ Not detected by MS or not confirmed by matching relative retention times on two columns.

d/ Detected as mixture.

e/ Corrected for 81% recovery.

f/ Value from rapid determination procedure.

g/ Detected as extractable organic compound.

h/ Detected as volatile organic compound.

i/ Not associated with EPN production process.

TABLE 18. ACID ANALOGS OF IDENTIFIED ESTERS IN EPN PRODUCTION PLANT WASTEWATER[a]

Compound identified	Acid analog
O-Methyl-S-ethyl phenylphosphonothioate	O-Hydrogen-S-ethyl phenylphosphonothioate
O-Ethyl-S-methyl phenylphosphonothioate	O-Ethyl-S-hydrogen phenylphosphonothioate
O,O-Dimethyl phenylphosphonate	O,O-Dihydrogen phenylphosphonate O-Methyl-O-hydrogen phenylphosphonate[b]
O-Ethyl-O-methyl phenylphosphonate	O-Ethyl-O-hydrogen phenylphosphonate
O,S-Dimethyl phenylphosphonothioate	O,S-Dihydrogen phenylphosphonothioate O-Methyl-S-hydrogen phenylphosphonothioate[b] O-Hydrogen-S-methyl phenylphosphonothioate

[a] Not process wastewater.

[b] The acid analog which is listed in Table 17; the true identity could be any of the listed analogs.

(10) O-Ethyl phenlyphosphonochlorothioate is an intermediate in the EPN production process which would not be expected to be stable for extended periods in an aqueous system.

(1) O-Hydrogen S-ethyl phenylphosphonothioate, (3) O-methyl-O-hydrogen phenylphosphonate, (5) O-methyl S-hydrogen phenylphosphonothioate, (6) O-methyl S-ethylphenylphosphonothioate, (8) O,O-diethyl phenylphosphonothioate, (9) O,O-dimethyl phenylphosphonothioate, (11) O,S-diethyl phenylphosphonothioate, and (12) O,O-diethyl phenylphosphonate are all expected from the hydrolysis and/or oxidation of EPN or the side products of the synthesis reaction.

The two concentration values reported for (15) O-(4-nitrophenyl) O-ethyl phenylphosphonothioate (EPN) are evidence of degradation during a month's storage at 4°C.

The presence of (7) O,O-diethyl chlorophenylphosphonothioate, (20), (21) dichlorobenzene, (22) trichlorobenzene, (25) 2-chlorobiphenyl, (30) 1,2-dichloroethylene, (31) 1,2-dichloroethane, (32) chloroform, and (35) chlorobenzene is strong evidence for the existence of a strong chlorinating agent in the untreated effluent.

(29) Diethyl ether, (33) benzene, and (34) toluene are process solvents associated with the manufacture of organic compounds.

(28) Ethanol is a starting material for the synthesis of EPN.

(36) Diethyl disulfide might result from the dimerization of ethyl sulfide, a hydrolysis product of S-ethyl phenylphosphonothioates.

(26) 2,4-Dichlorophenol is a predicted degradation product of O-dichlorophenyl phenylphosphonothioate, a compound closely related to leptophos.

(23) Biphenyl cannot be directly associated with the EPN production process but might have resulted from an upset condition involving heat-transfer fluid.

METHODS DEVELOPMENT

The bulk of analytical methods development for this program was carried out on synthetic samples consisting of water solutions of model compounds representative of various compound classes expected to be in actual waste effluent and one "protocol" sample taken from the azinphos-methyl/disulfoton production plant. Improvements and modifications in procedures, e.g., adjustment of gas chromatographic parameters, mass spectral extracted ion current plots, and the use of a nitrogen selective detector, required by differences in production and treatment processes were made throughout the project.

Extraction and Partitioning of Model Compounds

The partitioning scheme (Figure 1) was designed both to give some preliminary chemical characterization, and to simplify gas chromatographic analyses by isolating specific classes of compounds. Examples of such compound classes are: hydrolyzed esters which require derivatization (Fraction A) and nitrogen-containing organic bases (Fraction D).

The model compounds and their distribution and recovery from a synthetic sample as determined by GC/FPD detection are shown in Table 19.

TABLE 19. DISTRIBUTION AND RECOVERY OF ORGANOPHOSPHORUS COMPOUNDS

	Recovery (%)				
	Fraction				
Compound	A	D	J	AD	Total
Pesticides					
Ethion	-	4	144	-	148
Azinphos-methyl[a]	-	-	-	-	0
Demeton O	72	30	-	-	102
Alkyl esters					
Triethyl phosphate	46	30	18	-	94
O,O-Diethyl ethyl phosphonothioate	4	3	100	-	107
Hydrolyzed esters					
O-Methyl-O,O-dihydrogen phosphate	-	-	-	96	96
O-Ethyl-O,O-dihydrogen phosphate	-	-	-	65	65
O-Ethyl-S-hydrogen methylphosphonothioate	-	-	-	118	118

[a] The inability to recover azinphos-methyl was due to the poor chromatographic properties of this pesticide on the columns used.

In addition to the recovery data obtained on model compounds prior to sampling, distilled water was fortified with the pesticide produced at each site and analyzed in parallel with the wastewater samples. The results are summarized in Table 20.

TABLE 20. PESTICIDE RECOVERY DATA

Product	Level of fortification	% Recovery
Diazinon	10 μg/liter	69
Methyl parathion	10 μg/liter	76
Disulfoton	10 μg/liter	11[a]
Fonofos	10 μg/liter	85
EPN	100 μg/liter	81

[a] The 11% recovery value was obtained for the fortified sample run in the same manner as the wastewater. Further studies showed that the partitioning efficiency was 85% but that even with slow controlled concentration in Kuderna-Danish evaporators, losses at this step reduced the overall recovery to 34%.

In general, the results indicated a quantitative partitioning of hydrolyzed esters and the pesticides into Fractions A and J, respectively. The results of the partitioning of the nonhydrolyzed esters indicated that triethyl phosphate was present in all fractions with approximately 50% in Fraction A (water soluble) whereas the phosphonothioate was detected (100% of 107% total) in Fraction J (water insoluble). The hydrolyzed esters were not detected in Fraction A because they do not elute from the chromatographic column unless derivatized; hence the recovery of the acids are indicated by the results of the derivatized A fraction (AD) only.

The hydrolyzed alkyl esters used in the model sample, and their diazomethane esterification products, were analyzed by GC/MS to determine what impurities were present in the standards and to verify the identity and number of esterification products observed by GC/FPD.

No chromatographable compounds were observed in the nonesterified acids (Fraction A).

The results of the GC/MS analysis of esterified acids indicated that the esterification with diazomethane yielded the expected products. Minor quantities of other esters were detected in the esterified methyl phosphate and ethyl phosphate. These compounds were most likely due to esterification of impurities originally present in the standards and not due to multiple products from pure monoalkyl phosphates.

TLC procedures were also used to determine the partitioning of the model compounds in a fortified water sample. The results generally agreed with the GC/FPD with respect to the distribution of the model compounds among the three fractions. The few exceptions are discussed below.

O,O-Diethyl ethylphosphonothioate was not detected in any of the fractions. This compound volatilized from the plate prior to visualization. Azinphos-methyl was detected in Fractions A and J whereas the GC/FPD results showed azinphos-methyl only after derivatization. The TLC results for azinphos-methyl was verified by FMIR and suggests that the GC analysis was anomolous rather than loss of azinphos-methyl during extraction.

TLC is useful in the analysis of nonvolatile phosphorus-containing compounds. The following information may be obtained for individual compounds isolated from matrix interferences by preparative TLC.

Result	Compound information
R_f values in three solvent systems	Chemical classification
R_f standard data base match	Tentative identification
Preparative TLC/FMIR of isolated compound	Tentative identification
Preparative TLC/FMIR standard match	Confirmation
Preparative TLC/Direct inlet mass spectrum	Identification/confirmation

Derivatization of Organophosphorus Acids

Hydrolyzed organophosphorus esters, major pesticide degradation products, are not sufficiently volatile for direct GC analysis. A portion of each model extract was derivatized with diazomethane to produce methyl esters of these hydrolysis products. Prior to analysis of these derivatized extracts the efficiency of the esterification reaction was determined for the following compounds.

Compound	Conversion product	% Conversion
O-Methyl-O,O-dihydrogen phosphate	O,O,O-Trimethyl phosphate	96
O-Ethyl-O,O-dihydrogen phosphate	O-Ethyl-O,O dimethyl phosphate	68
O-Ethyl-S-hydrogen methyl phosphonothioate	O-Ethyl-S-methyl methylphosphonothioate	45

The efficiencies are based on the standards being 100% pure. TLC analyses of each of the standards showed at least one major impurity in the ethyl phosphate and the phosphonothioate which might explain the apparent low conversion rate.

Several problems were associated with the GC analysis of hydrolyzed esters. Poor chromatographic separation and questionable stability of methyl derivatives, have been investigated by Shafik et al.[8] Synthesis of amyl derivatives was recommended for better chromatographic resolution. However, the longer retention times of the amyl esters might cause coelution with other higher molecular weight phosphorus compounds. Amyl esterification would provide an esterifying agent whose carbon number exceeds that of the pesticides' alkyl groups and allow one to distinguish between monoalkyl and dialkyl phosphates after derivatization.

The presence of the organophosphorus acids has an adverse effect on the analysis of the water soluble esters which also partition into Fraction A. Deposition of the acids on the head of the chromatographic column often prevents the elution of the normally volatile esters. Because the esters are at least partially lost during evaporative steps in derivatization, attempts were made to separate these compounds from the acids prior to esterification. Preliminary efforts to partition the water-soluble esters from protocol Fraction A into ether resulted in incomplete separation of the two compound classes. A different approach might be to extract both esters and acids into a nonaqueous medium compatible with the esterification reaction to thus avoid evaporative losses and differentiate between the derivatized esters and those present before derivatization by prudent choice of the aklylating agent. The most promising approach would be to separate the acids from the water soluble esters with a strong ion-exchange resin. Verweij and Boter have reported[9] the separation of methylphosphoric acids on BIORAD AG 1-X8.

Analysis of the "Protocol" Sample

All fractions of the "protocol" sample (2004) were developed in three TLC solvents: ethanol, acetone/ethyl acetate, and methylene chloride/cyclohexane.

Fraction A was found to contain at least 10 phosphorus-containing compounds at an approximate concentration of 20 ppm each with respect to the original effluent sample; Fraction J had a minimum of three phosphorus compounds at this concentration level; and no phosphorus compounds were detected in Fraction D. The R_f matches in all three solvents with standards in the MRI data base are summarized in Table 21.

Phosphonothioates and dithioates predicted for this site were entered into a data matching program. Identification based on matching R_f values is

TABLE 21. R_f MATCHES[a] FOR "PROTOCOL" SAMPLE (2004)

Fraction	Matching standard
2004 A	Methyl phosphonic acid[b] Monomethyl phosphate Dimethyl phosphate Ethyl methyl phosphonic acid[b] Diethyl phosphate Triethyl phosphate Diethyl ethylphosphonate[b] Diisopropyl methylphosphonate[b]
2004 AD[c]	Dimethyl phosphate Diethyl ethylphosphonate[b] O-Ethyl S-methyl methylphosphonothioate[b] Triethyl phosphate
2004 D	None
2004 J	Dimethyl phosphate Tri-N-butyl phosphate Azinphos-methyl

---

[a] The listed compounds have matching R_f values in three developing solvents: ethanol, acetone/ethyl acetate, and methylene chloride/cyclohexane.

[b] Not expected at this site.

[c] Derivatized with diazomethane.

Note: All compounds detected in Fraction A were not detected in AD because the more volatile esters are lost during evaporation to dryness. The AD fraction is designed to detect only the compounds that are originally present as acids.

the least reliable identification in the analytical scheme. Generally, R_f matching was used as supporting information for GC/FPD, FMIR, and GC/MS identification.

"Protocol" Fraction A (2004 A), derivatized Fraction A (2004 AD) and the methanol eluate of a preparative TLC band from 2004 A at R_f 0.73, ethanol, and 0.35 to 0.45, acetone/ethyl acetate, were analyzed by GC/MS using the Carbowax 20M column. The organophosphorus compounds identified in these extracts are listed in Table 22.

Other fractions of the protocol sample were not analyzed by GC/MS because of the additional time and effort involved. The purpose of the protocol sample was to test and evaluate the analytical methodology. The results obtained on the limited number of extracts analyzed indicated that compounds could be identified and wastewater effluents characterized by the methodology applied to the protocol samples.

Recommended Procedural Modifications

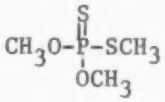
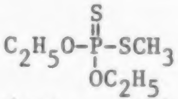
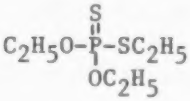
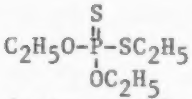
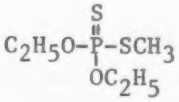
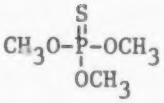
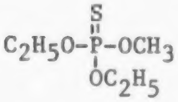
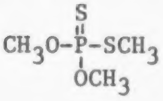
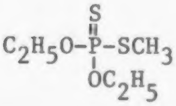
In addition to the modifications to specific procedures already mentioned in this section, some general recommendations can be made to improve the overall sampling and analysis scheme.

Studies should be done to determine evaporation and degradation losses in both the aqueous sample and the organic extract during storage prior to analysis. Efforts should be made to preserve the integrity of those compounds most likely to impact on the environment.

Sufficient final effluent sample should be collected either in volume or by means of accumulators to compensate for the dilution factor commonly seen between untreated waste streams and the treated discharge. In addition, all samples collected from streams should be on a flow proportional rather than time proportional basis.

In a survey project where all samples are to be characterized by GC/MS with emphasis given to specific element-containing (e.g., phosphorus) compounds, a GC prescreen employing a column effluent splitter with FID and FPD detectors would be desirable. This would allow determination of concentration ratios of phosphorus and nonphosphorus-containing compounds. These data would facilitate decisions on the need for further extract concentration and/or cleanup prior to GC/MS analysis and in turn maximize the number of interpretable spectra of organophosphorus compounds. It is also suggested that a FPD detector be used in parallel with the GC/MS in identification of phosphorus compounds.

TABLE 22. ORGANOPHOSPHORUS COMPOUNDS IDENTIFIED IN PROTOCOL SAMPLES

Sample	Compounds identified
2004 A	 $\mathrm{CH_3O{-}\underset{OCH_3}{\overset{S}{\overset{\|}{P}}}{-}SCH_3}$
	 $\mathrm{C_2H_5O{-}\underset{OC_2H_5}{\overset{S}{\overset{\|}{P}}}{-}SCH_3}$ (major peak)
	 $\mathrm{C_2H_5O{-}\underset{OC_2H_5}{\overset{S}{\overset{\|}{P}}}{-}SC_2H_5}$
2004 A, R_f 0.73, ethanol, and R_f 0.35 to 0.45 acetone/ethyl acetate	 $\mathrm{C_2H_5O{-}\underset{OC_2H_5}{\overset{S}{\overset{\|}{P}}}{-}SC_2H_5}$ (major peak)
	 $\mathrm{C_2H_5O{-}\underset{OC_2H_5}{\overset{S}{\overset{\|}{P}}}{-}SCH_3}$
2004 AD	 $\mathrm{CH_3O{-}\underset{OCH_3}{\overset{S}{\overset{\|}{P}}}{-}OCH_3}$
	 $\mathrm{C_2H_5O{-}\underset{OC_2H_5}{\overset{S}{\overset{\|}{P}}}{-}OCH_3}$
	 $\mathrm{CH_3O{-}\underset{OCH_3}{\overset{S}{\overset{\|}{P}}}{-}SCH_3}$
	 $\mathrm{C_2H_5O{-}\underset{OC_2H_5}{\overset{S}{\overset{\|}{P}}}{-}SCH_3}$

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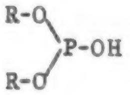
8. Shafik, T., D. E. Bradway, H. F. Enos and A. R. Yobs, Journal of Agricultural and Food Chemistry 21:625-629, 1973.

9. Verweij, A., and H. L. Boter, Chemical Laboratorium TNO Report No. 1976-19, Rijswijk, The Netherlands, 1976.

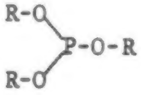
APPENDIX A: NOMENCLATURE

GENERAL IUPAC NOMENCLATURE FOR ORGANOPHOSPHORUS COMPOUNDS

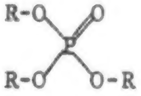
O,O-Dialkyl phosphorous acid



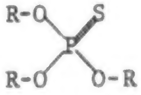
Trialkyl phosphite



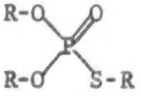
O,O,O-Trialkyl phosphate



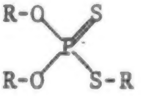
O,O,O-Trialkyl phosphorothioate



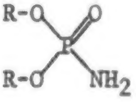
O,O-Dialkyl S-alkyl phosphorothioate



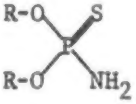
O,O-Dialkyl S-alkyl phosphorodithioate



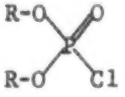
O,O-Dialkyl phosphoroamidate



O,O-Dialkyl phosphoroamidothioate



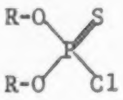
O,O-Dialkyl phosphorochloridate



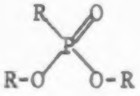
(continued)

GENERAL IUPAC NOMENCLATURE FOR ORGANOPHOSPHORUS COMPOUNDS (concluded)

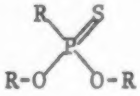
O,O-Dialkyl phosphorochlorothioate



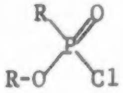
O,O-Dialkyl phosphonate



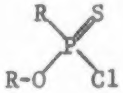
O,O-Dialkyl phosphonothioate



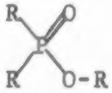
O-Alkyl phosphonochloridate



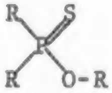
O-Alkyl phosphonochlorothioate



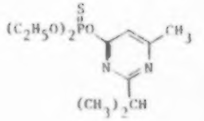
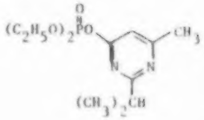
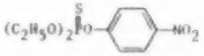
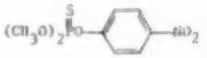
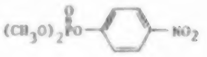
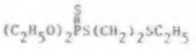
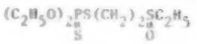
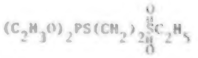
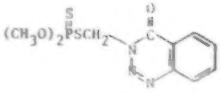
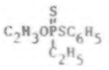
O-Alkyl phosphinate



O-Alkyl phosphinothioate

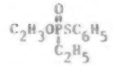
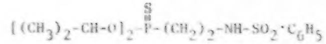
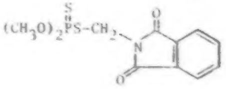
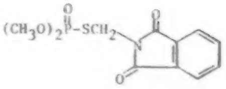
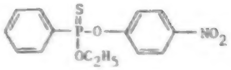
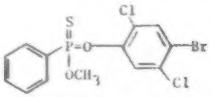
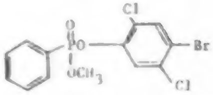
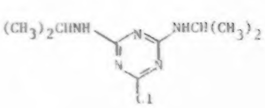


NOMENCLATURE OF PESTICIDES, RELATED OXYGENATED COMPOUNDS AND ORGANOPHOSPHORUS COMPOUNDS

Common name	Trade name	Chemical name	Structure
Diazinon	Spectracide	0,0-Diethyl O-[6-methyl-2-(1-methylethyl)]-4-pyrimidinyl phosphorothioate	
Diazoxon		0,0-Diethyl O-[6-methyl-2-(1-methylethyl)]-4-pyrimidinyl phosphate	
Ethyl parathion	**Niran**	**0,0-Diethyl O-(4-nitrophenyl) phosphorothioate**	
Methyl parathion	**Metacide**	**0,0-Dimethyl O-(4-nitrophenyl) phosphorothioate**	
Methyl paraoxon		**0,0-Dimethyl O-(4-nitrophenyl) phosphate**	
Disulfoton	**Di-Syston**	**0,0-Diethyl S-[2-(ethylthio)ethyl] phosphorodithioate**	 $(C_2H_5O)_2\overset{\overset{S}{\|}}{P}S(CH_2)_2SC_2H_5$
Oxydisulfoton	**Di-Syston sulfoxide**	**0,0-Diethyl S-[2-(ethylsulfinyl)ethyl] phosphorodithioate**	 $(C_2H_5O)_2\underset{\underset{S}{\|}}{P}S(CH_2)_2\underset{\underset{O}{\|}}{S}C_2H_5$
Disulfoton sulfone	Di-Syston sulfone	0,0-Diethyl S-[2-(ethylsulfonyl)ethyl] phosphorodithioate	 $(C_2H_3O)_2PS(CH_2)_2\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}C_2H_5$
Azinphos-methyl	Guthion	0,0-Dimethyl S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)-methyl] phosphorodithioate	
Fonofos	Dyfonate	O-Ethyl S-phenyl ethylphosphonodithioate	 $C_2H_3O\overset{\overset{S}{\|}}{\underset{\underset{C_2H_5}{\vert}}{P}}SC_6H_5$

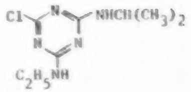
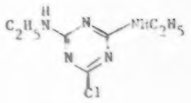
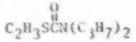
(continued)

NOMENCLATURE OF PESTICIDES, RELATED OXYGENATED COMPOUNDS AND ORGANOPHOSPHORUS COMPOUNDS (continued)

Common name	Trade name	Chemical name	Structure
Fonofoxon		O-Ethyl S-phenyl ethylphosphonothioate	 $C_2H_3O\overset{O}{\underset{C_2H_5}{P}}SC_6H_5$
Bensulide	Betasan	O,O-bis(1-Methyl) S-{2-[(phenylsulfonyl)amino]ethyl} phosphorodithioate	 $[(CH_3)_2-CH-O]_2-\overset{S}{P}-(CH_2)_2-NH-SO_2\cdot C_6H_5$
Phosmet	Imidan	S-[(1,3-Dihydro-1,3-dioxo-2H-isoindol-2-yl)methyl] O,O-dimethyl phosphorodithioate	
Phosmet oxygen analog		N-(Mercaptomethyl)phthalimide S-(O,O-dimethyl) phosphorothioate	
EPN		O-(4-nitrophenyl) O-ethyl phenylphosphonothioate	
Leptophos	Phosvel	O-(4-Bromo-2,5-dichlorophenyl) O-methyl phenylphosphonothioate	
Leptophoxon		O-(4-Bromo-2,5-dichlorophenyl) O-methyl phenylphosphonate	
Propazine	Milogard	2-Chloro-4,5-bis(isopropylamino)-S-triazine	

(continued)

NOMENCLATURE OF PESTICIDES, RELATED OXYGENATED COMPOUNDS AND ORGANOPHOSPHORUS COMPOUNDS (continued)

Common name	Trade name	Chemical name	Structure
Atrazine	Aatrex	6-Chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine	
Simazine	Princep	6-Chloro-N,N'-diethyl-1,3,5-trizine-2,4-diamine	
EPTC	Eptam	S-Ethyl dipropylcarbamothioate	 $C_2H_3S\overset{O}{\overset{\Vert}{C}}N(C_3H_7)_2$

APPENDIX B: MASS SPECTRA OF IDENTIFIED COMPOUNDS NOT PRESENT IN THE MSS* LIBRARY

Compound

Figure B-1. Mass spectrum of S,S-dimethyl hydrogen phosphite
Figure B-2. Mass spectrum of O,O-dimethyl phosphoramidothioate
Figure B-3. Mass spectrum of O-methyl-S-methyl phosphoramidothioate
Figure B-4. Mass spectrum of O-methyl-O-ethyl ethylphosphonate
Figure B-5. Mass spectrum of 1-thiol diethyl disulfide
Figure B-6. Mass spectrum of *p*-chlorobenzamide
Figure B-7. Mass spectrum of O,O,O-trimethyl phosphorothioate
Figure B-8. Mass spectrum of O,O-dimethyl-S-methyl phosphorothioate
Figure B-9. Mass spectrum of O,O-dimethyl phosphorochlorothioate
Figure B-10. Mass spectrum of 2-isopropyl-4-methoxy-6-methyl pyrimidine
Figure B-11. Mass spectrum of O,O-dimethyl-O-ethyl phosphorothioate
Figure B-12. Mass spectrum of O,O-dimethyl-S-methyl phosphorodithioate
Figure B-13. Mass spectrum of O-methyl-S,S-dimethyl phosphorodithioate
Figure B-14. Mass spectrum of 2-isopropyl-4-ethoxy-6-methyl pyrimidine
Figure B-15. Mass spectrum of O,O-diethyl ethylphosphonothioate
Figure B-16. Mass spectrum of O,O,O-triethyl phosphate
Figure B-17. Mass spectrum of O,O-diethyl-O-methyl phosphorothioate
Figure B-18. Mass spectrum of O,O-diethyl-S-methyl phosphorothioate
Figure B-19. Mass spectrum of O,O-dimethyl phenylphosphonate
Figure B-20. Mass spectrum of S-ethyl hexahydro-1H-azepine-1-carbothioate (molinate)
Figure B-21. Mass spectrum of O,O-diethyl phosphorochlorothioate
Figure B-22. Mass spectrum of S-ethyl dipropyl thiocarbamate (EPTC)
Figure B-23. Mass spectrum of O,O-diethyl-S-ethyl phosphorothioate
Figure B-24. Mass spectrum of O,O-diethyl-S-methyl phosphorodithioate
Figure B-25. Mass spectrum of O-methyl-O-ethyl phenylphosphonate
Figure B-26. Mass spectrum of O,O-dimethyl phenylphosphonothioate
Figure B-27. Mass spectrum of O-methyl-S-methyl phenylphosphonothioate
Figure B-28. Mass spectrum of S-propyl dipropyl thiocarbamate (vernolate)
Figure B-29. Mass spectrum of S-propyl butyl ethyl thiocarbamate (pebulate)
Figure B-30. Mass spectrum of O,O-diethyl-S-ethyl phosphorodithioate
Figure B-31. Mass spectrum of O,O-diethyl phenylphosphonate
Figure B-32. Mass spectrum of S-ethyl cyclohexylethyl thiocarbamate (cycloate)
Figure B-33. Mass spectrum of O-ethyl-S-methyl phenylphosphonothioate
Figure B-34. Mass spectrum of O-methyl-S-ethyl phenylphosphonothioate

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*Mass Spectral Search System, ADP Network Services, Cyphernetics Division, Copyright 1975.

Compound (concluded)

Figure B-35. Mass spectrum of O-ethyl phenylphosphonochlorothioate
Figure B-36. Mass spectrum of 2,4-bis(ethylamino)-6-ethylmercapto-S-triazine
Figure B-37. Mass spectrum of O-methyl-O,S-diisopropyl phosphorodithioate
Figure B-38. Mass spectrum of O,O-diisopropyl-S-methyl phosphorodithioate
Figure B-39. Mass spectrum of O,O-diethyl phenylphosphonothioate
Figure B-40. Mass spectrum of O,S-diethyl phenylphosphonothioate
Figure B-41. Mass spectrum of O-ethyl-S-phenyl ethylphosphonodithioate (fonofos)
Figure B-42. Mass spectrum of 2,6-di-tertbutyl-4-methoxymethyl phenol
Figure B-43. Mass spectrum of O,O-diethyl chlorophenylphosphonothioate
Figure B-44. Mass spectrum of O-(chloroaminophenyl)-O-methyl phenylphosphonate
Figure B-45. Mass spectrum of O-(4-nitrophenyl)-O-ethyl phenylphosphonothioate (EPN)
Figure B-46. Mass spectrum of O-(4-nitrophenyl)-O-ethyl chlorophenylphosphonothioate
Figure B-47. Mass spectrum of O-(chlorobromoaminophenyl)-O-methyl phenylphosphonate
Figure B-48. Mass spectrum of O-(chlorobromoaminophenyl)-O-ethyl phenylphosphonate

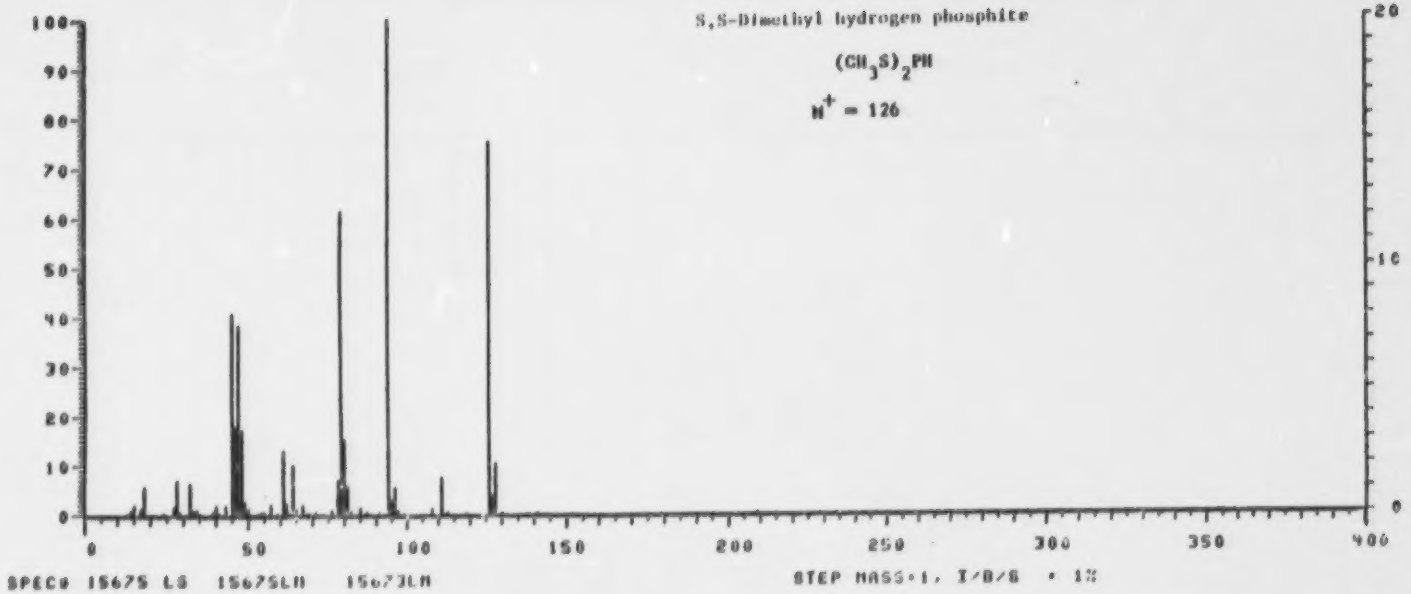

Figure B-1. Mass spectrum of S,S-dimethyl hydrogen phosphite.

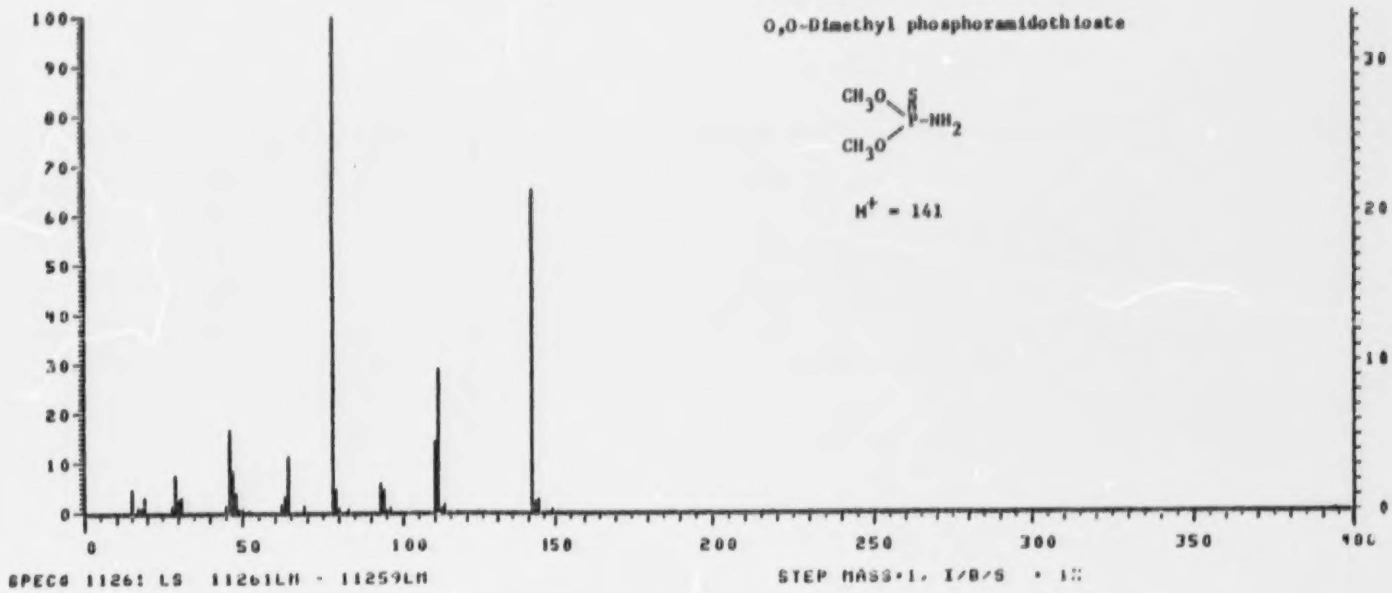

Figure B-2. Mass spectrum of O,O-dimethyl phosphoramidothioate.

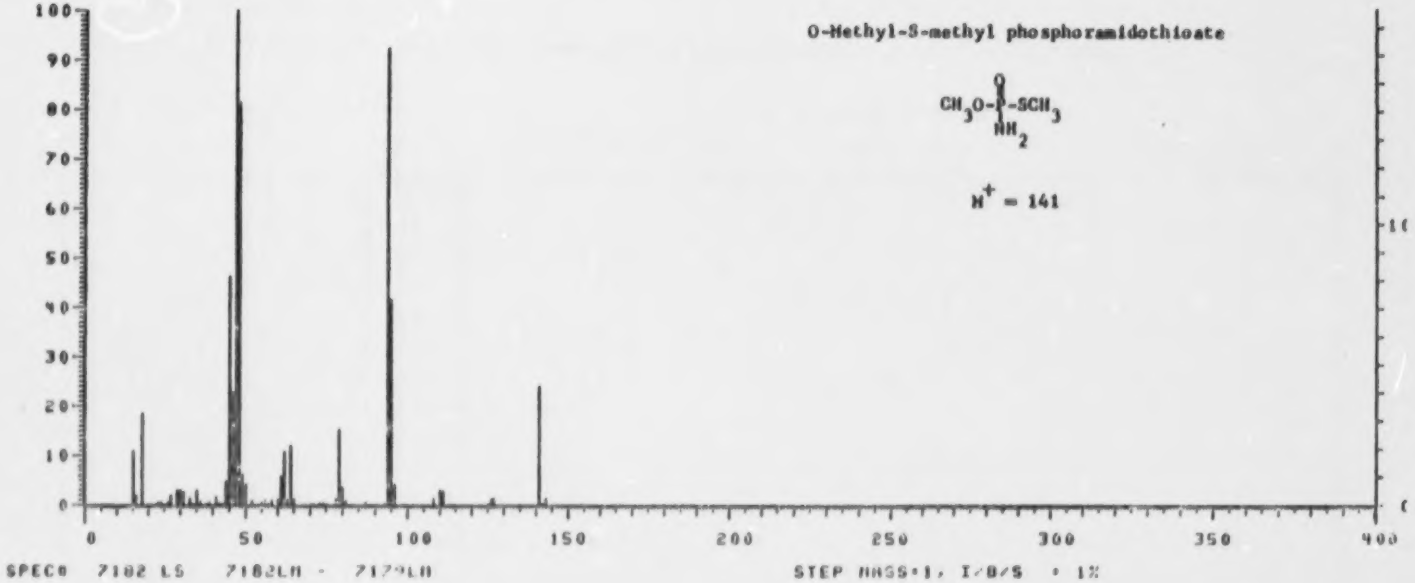

Figure B-3. Mass spectrum of O-methyl-S-methyl phosphoramidothioate.

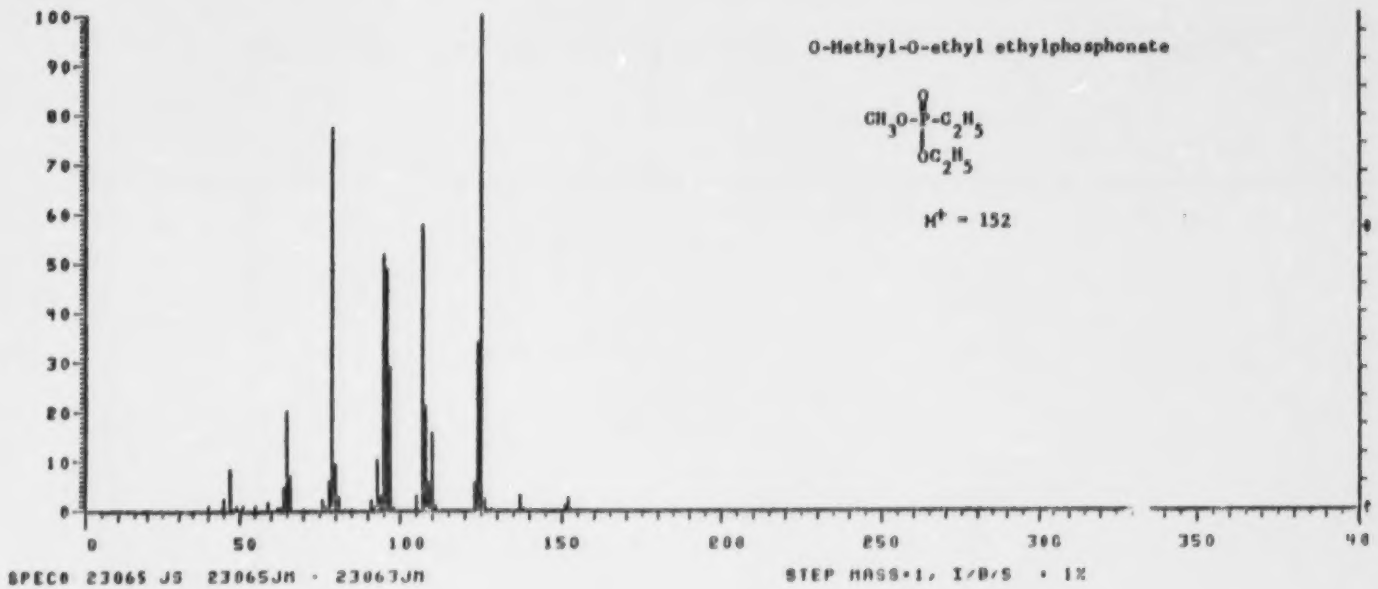

Figure B-4. Mass spectrum of O-methyl-O-ethyl ethylphosphonate.

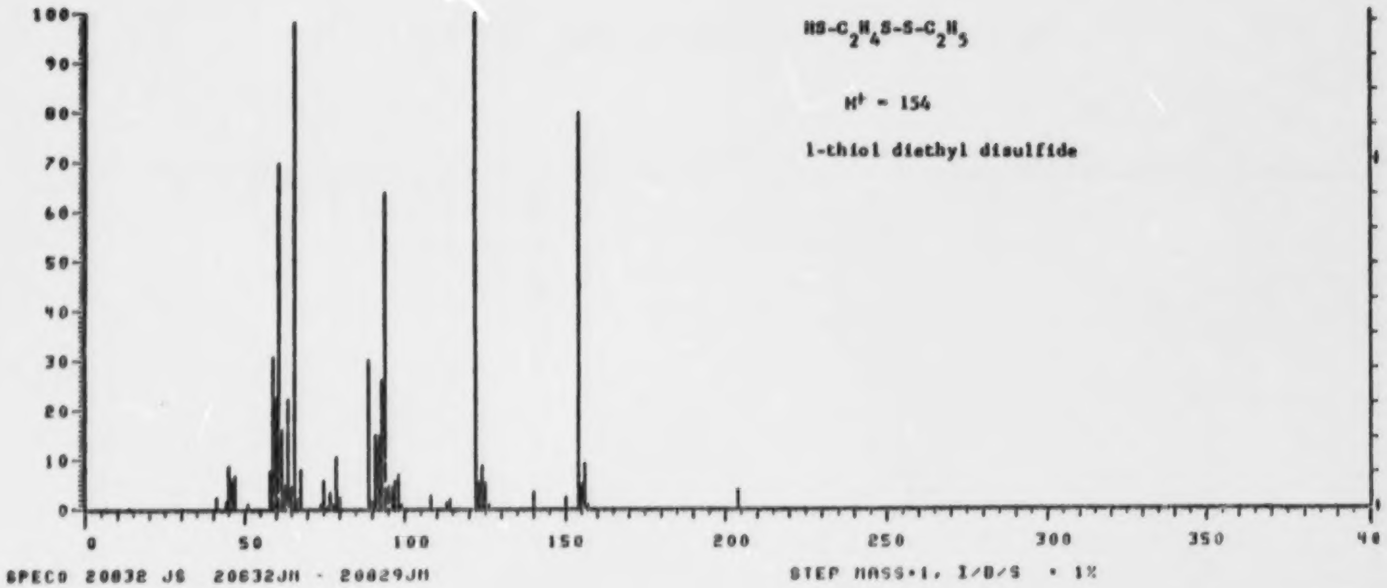

Figure B-5. Mass spectrum of 1-thiol diethyl disulfide.

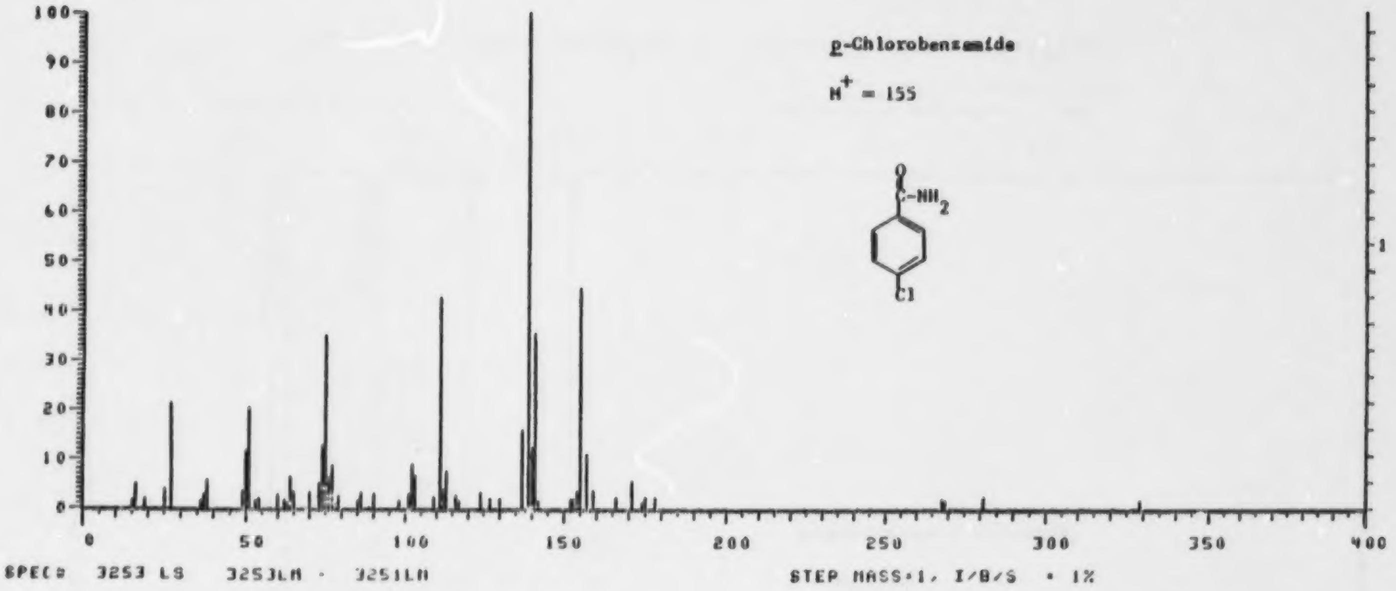

Figure B-6. Mass spectrum of p-chlorobenzamide.

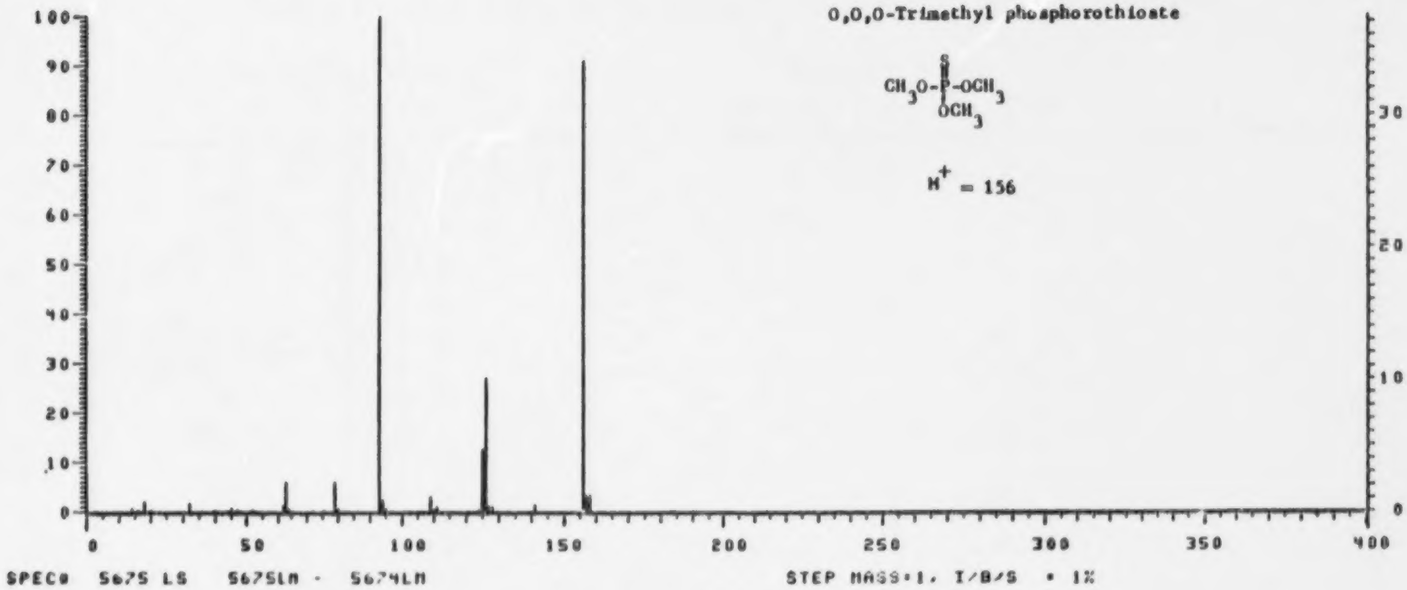

Figure B-7. Mass spectrum of O,O,O-trimethyl phosphorothioate.

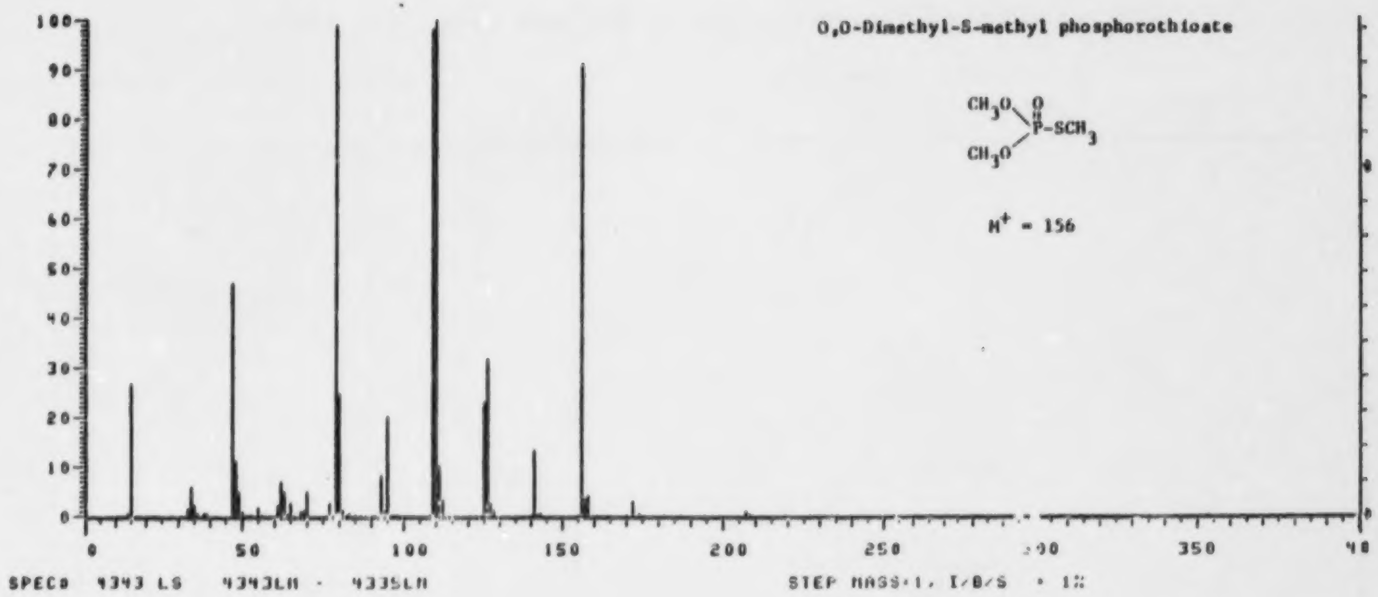

Figure B-8. Mass spectrum of O,O-dimethyl-S-methyl phosphorothioate.

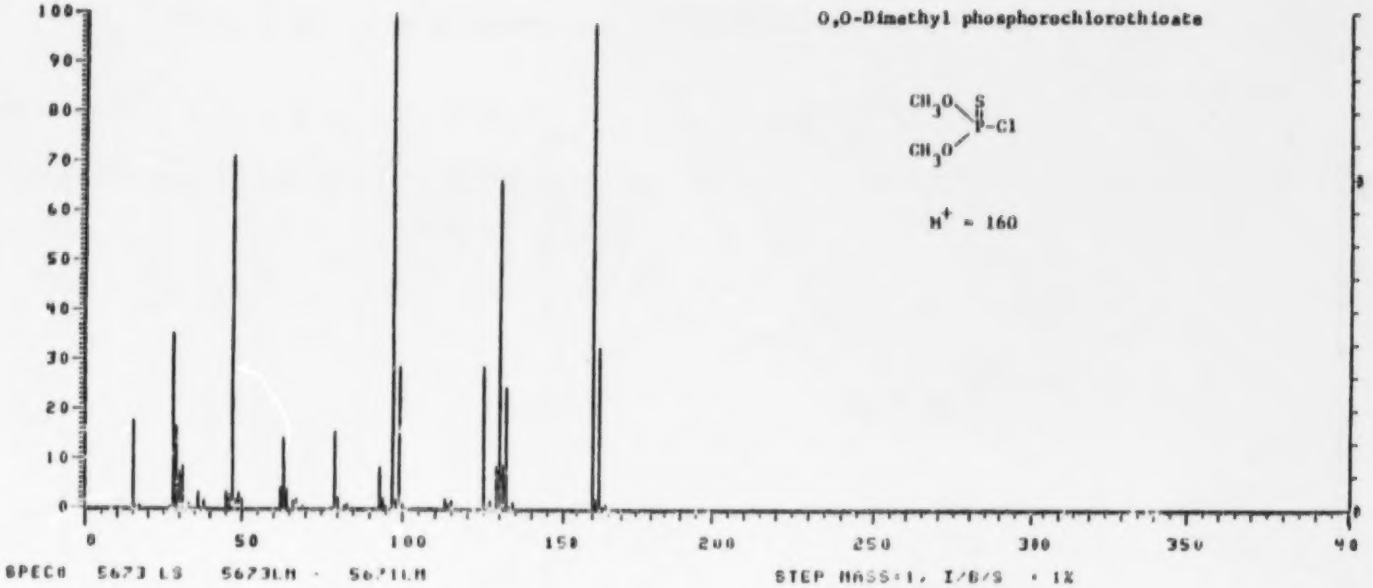

Figure B-9. Mass spectrum of O,O-dimethyl phosphorochlorothioate.

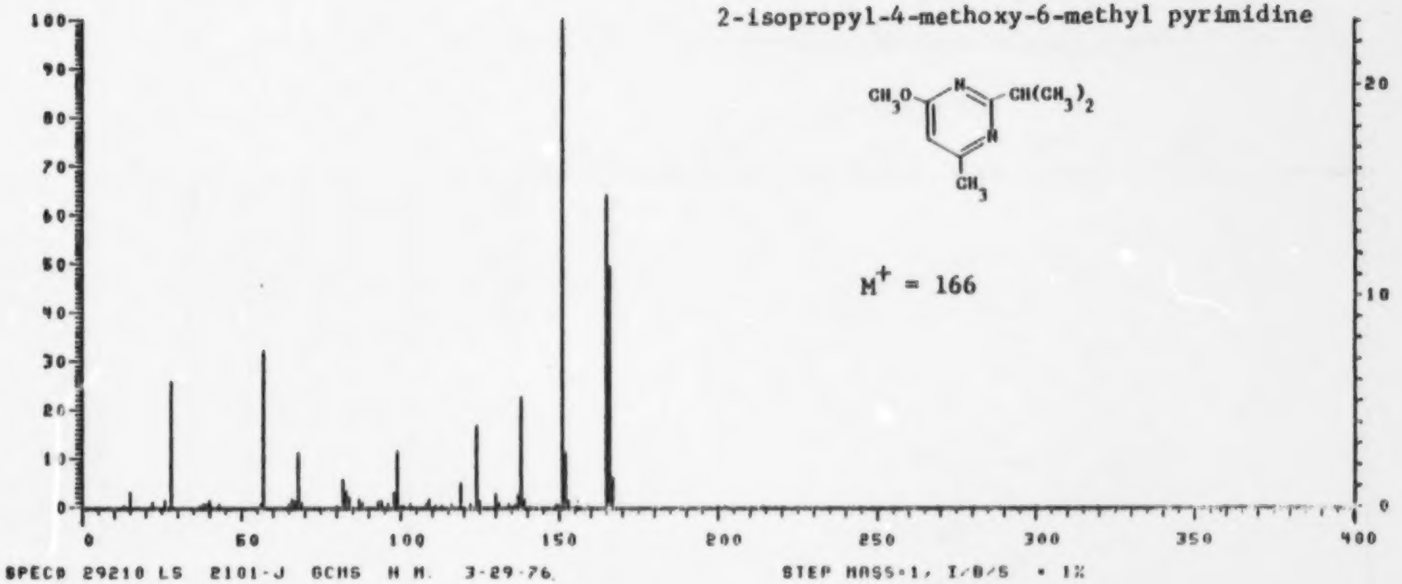

Figure B-10. Mass spectrum of 2-isopropyl-4-methoxy-6-methyl pyrimidine.

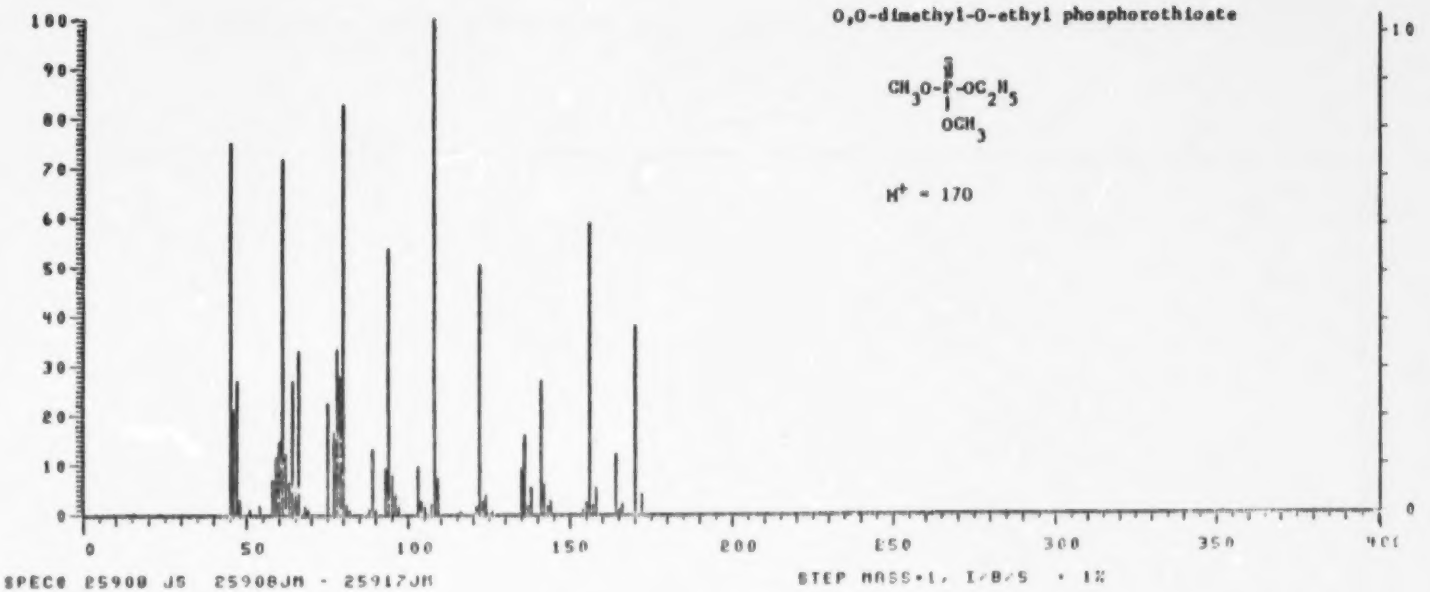

Figure B-11. Mass spectrum of O,O-dimethyl-O-ethyl phosphorothioate.

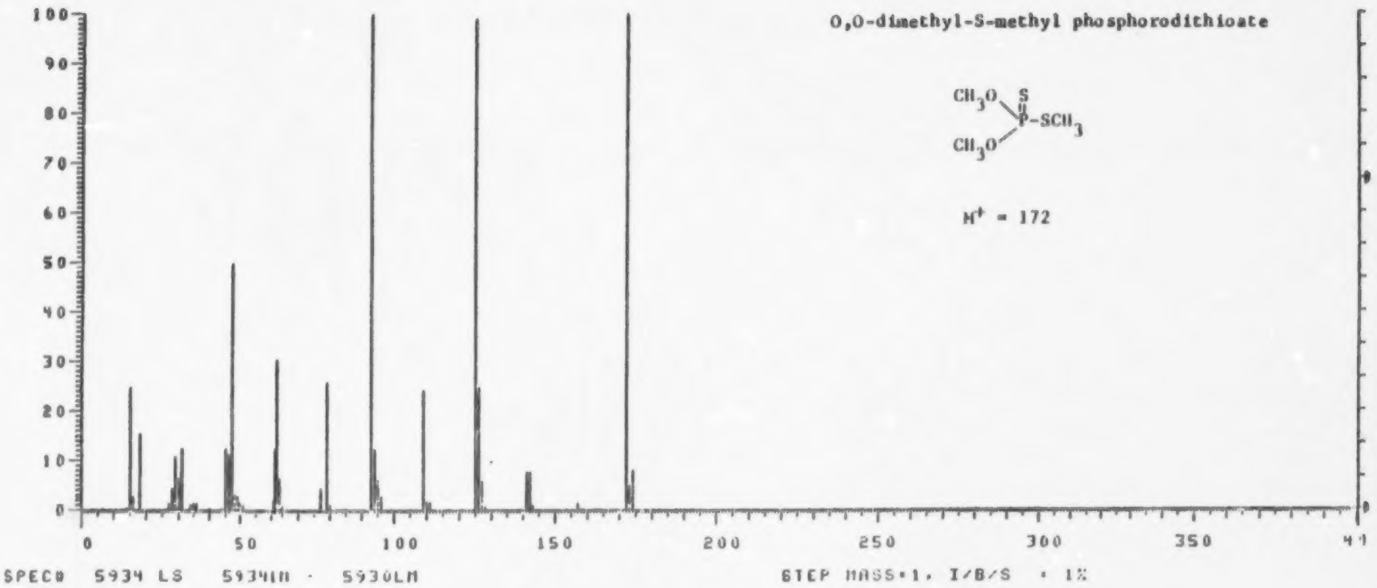

Figure B-12. Mass spectrum of O,O-dimethyl-S-methyl phosphorodithioate.

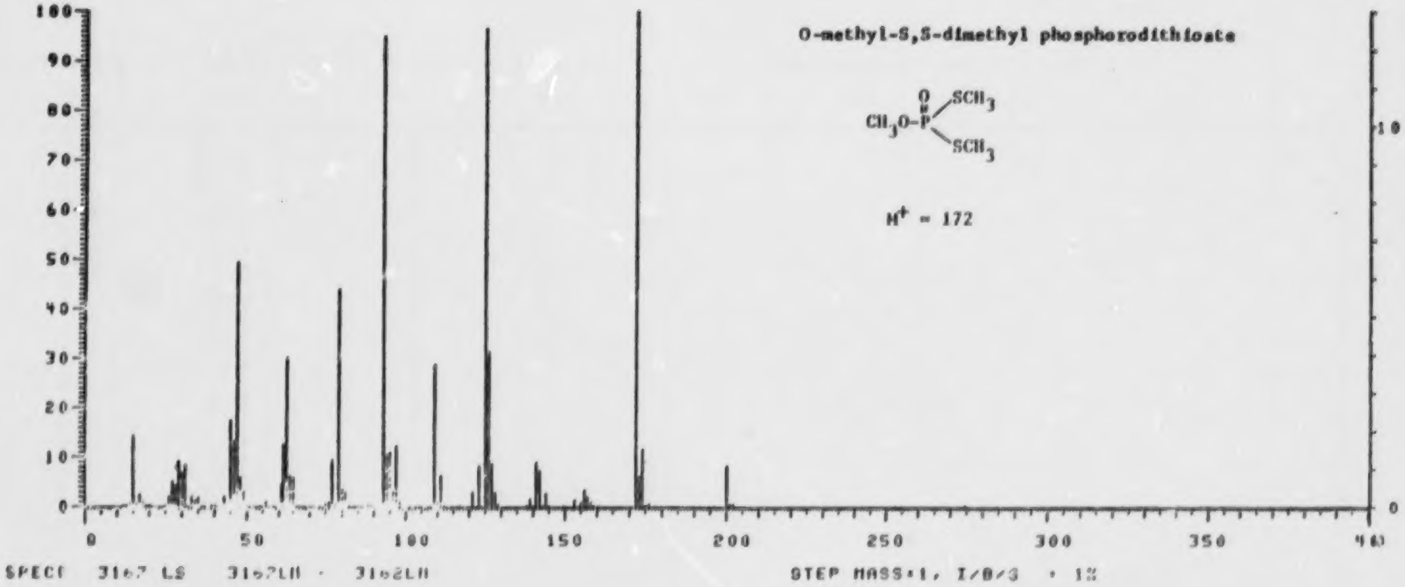

Figure B-13. Mass spectrum of O-methyl-S,S-dimethyl-phosphorodithioate.

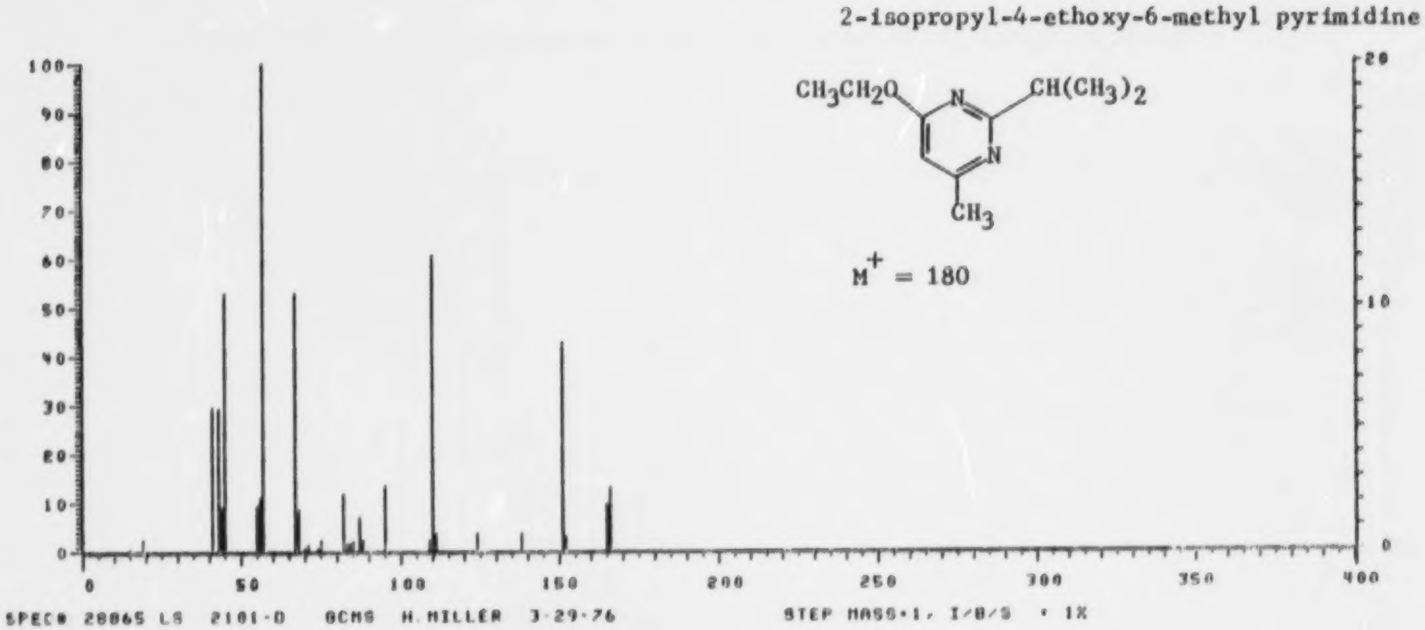

Figure B-14. Mass spectrum of 2-isopropyl-4-ethoxy-6-methyl pyrimidine.

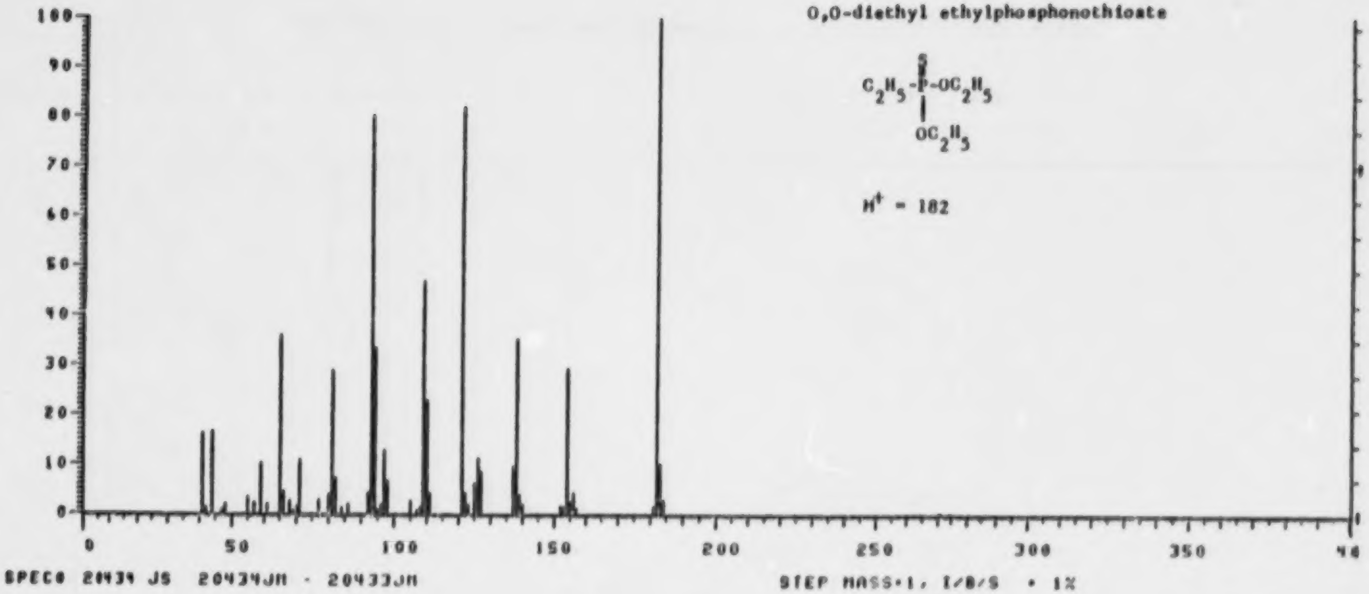

Figure B-15. Mass spectrum of O,O-diethyl ethylphosphonothioate.

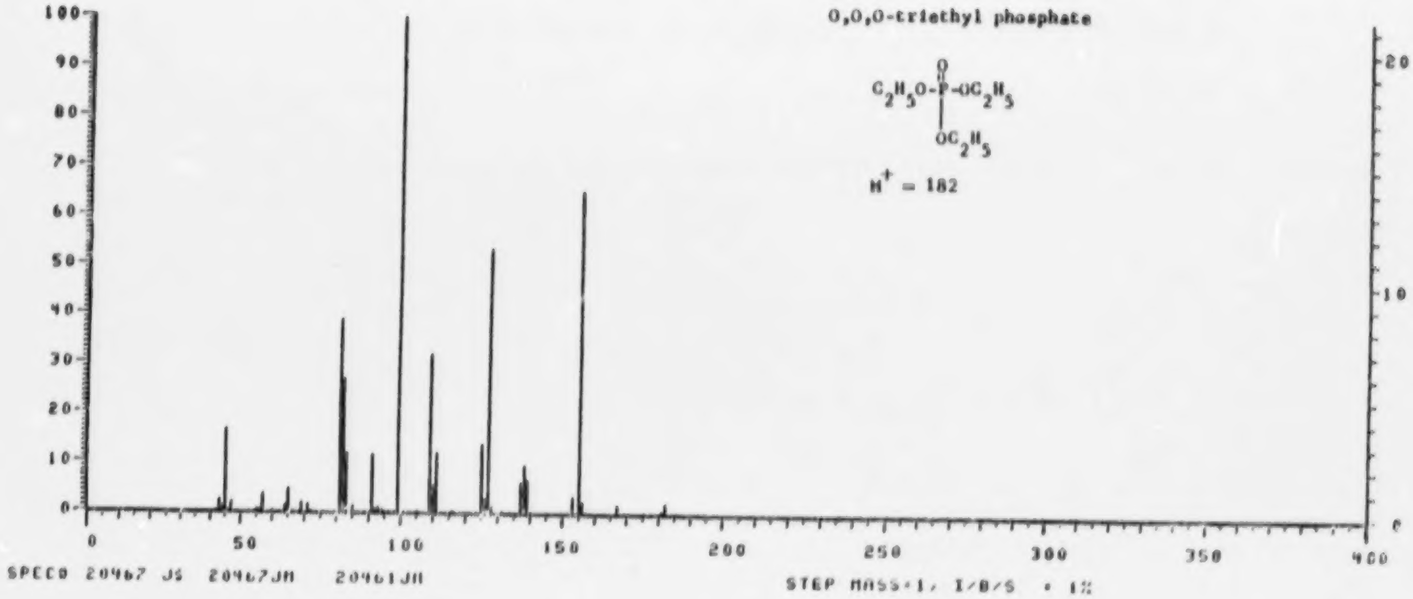

Figure B-16. Mass spectrum of O,O,O-triethyl phosphate.

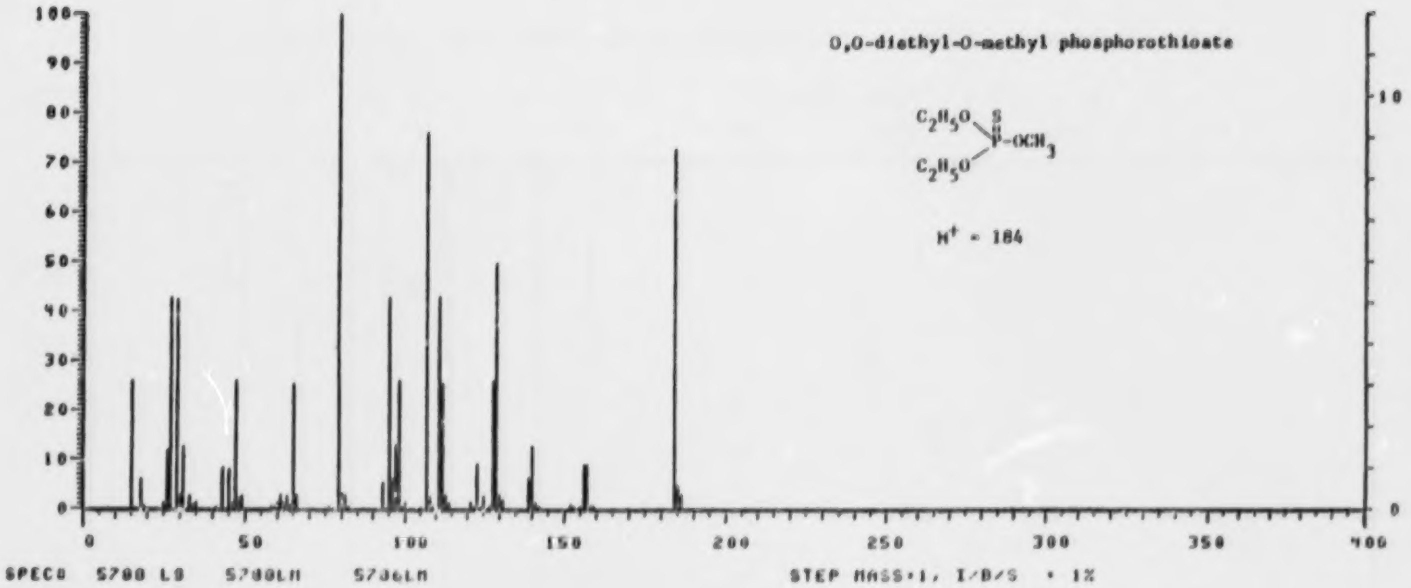

Figure B-17. Mass spectrum of O,O-diethyl-O-methyl phosphorothioate.

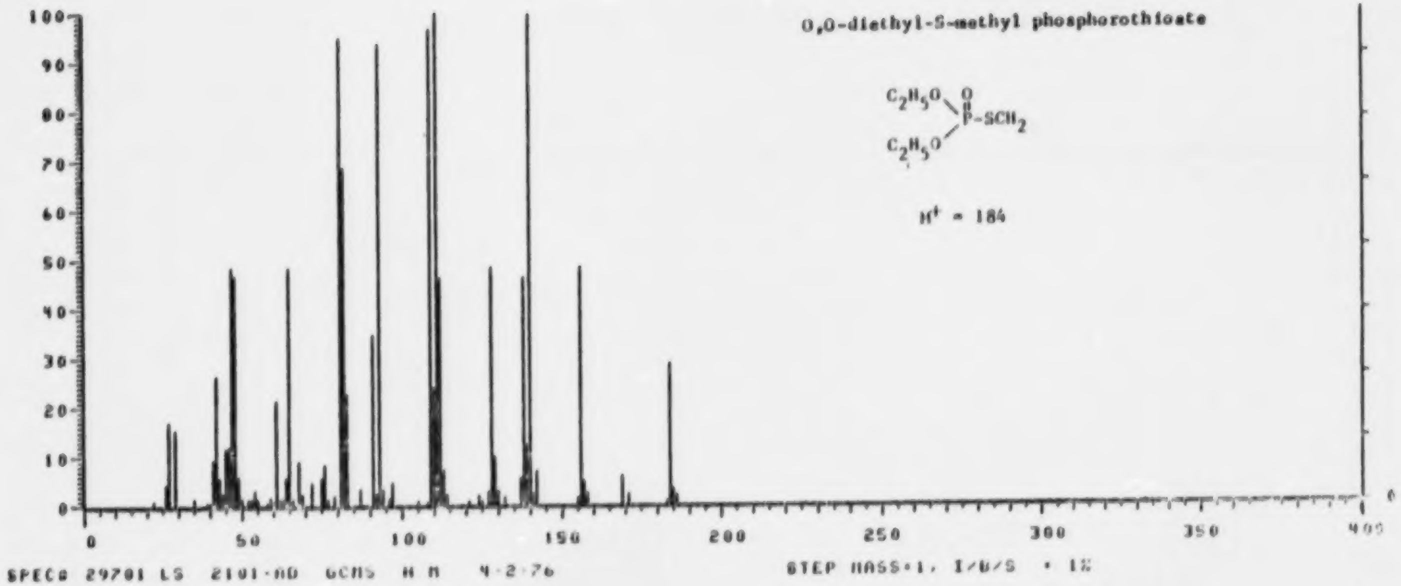

Figure B-18. Mass spectrum of O,O-diethyl-S-methyl phosphorothioate.

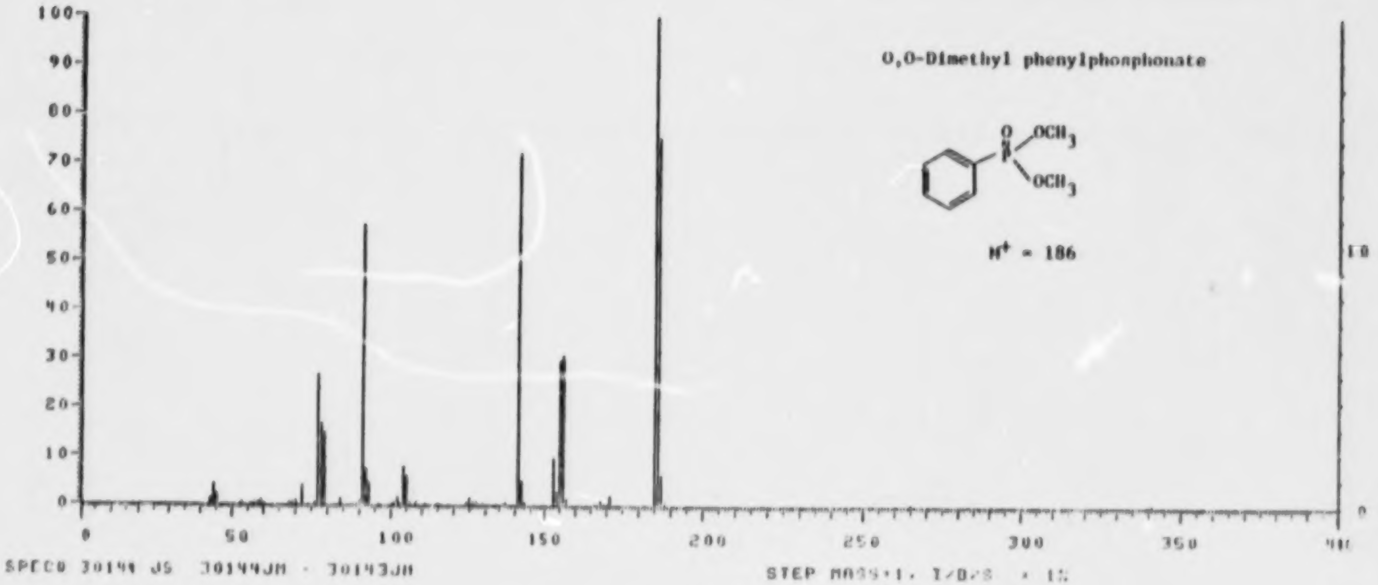

Figure B-19. Mass spectrum of O,O-dimethyl phenylphosphonate.

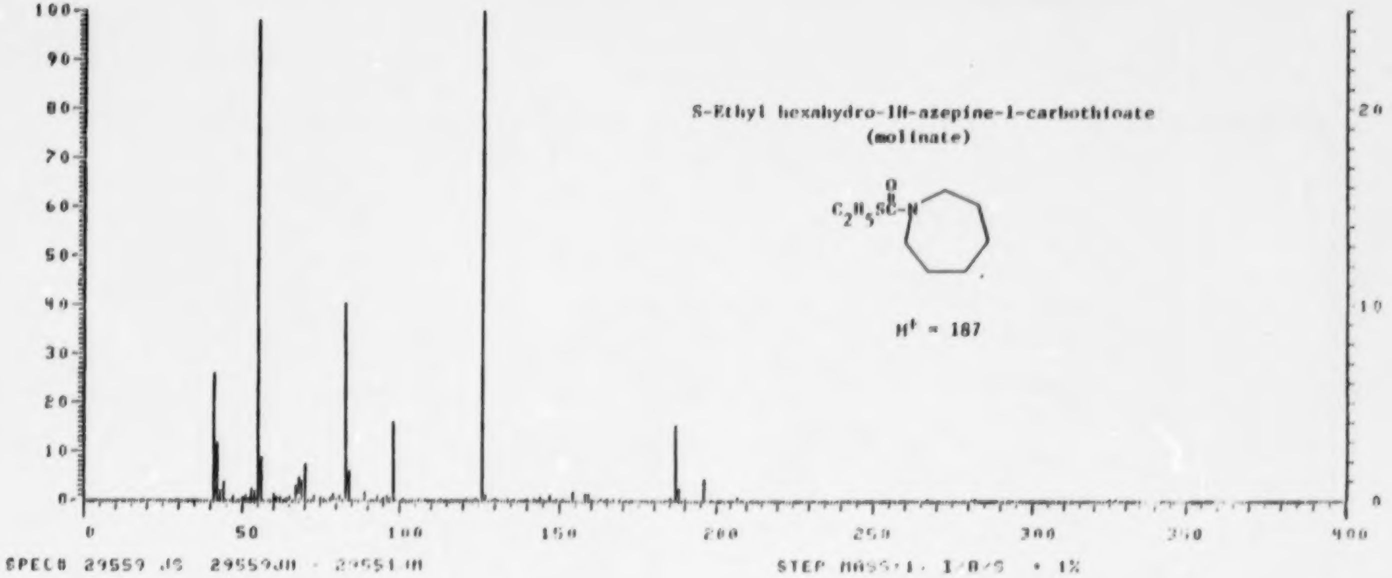

Figure B-20. Mass spectrum of S-ethyl hexahydro-1H-azepine-1-carbothioate (molinate).

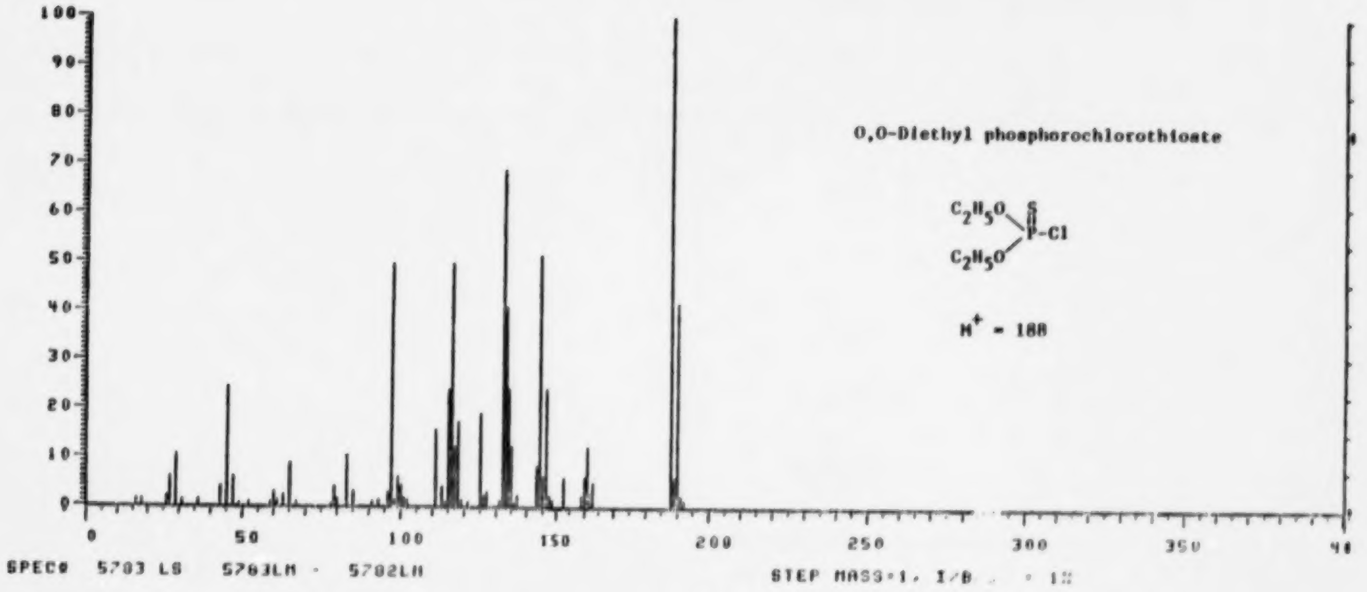

Figure B-21. Mass spectrum of O,O-diethyl phosphorochlorothioate.

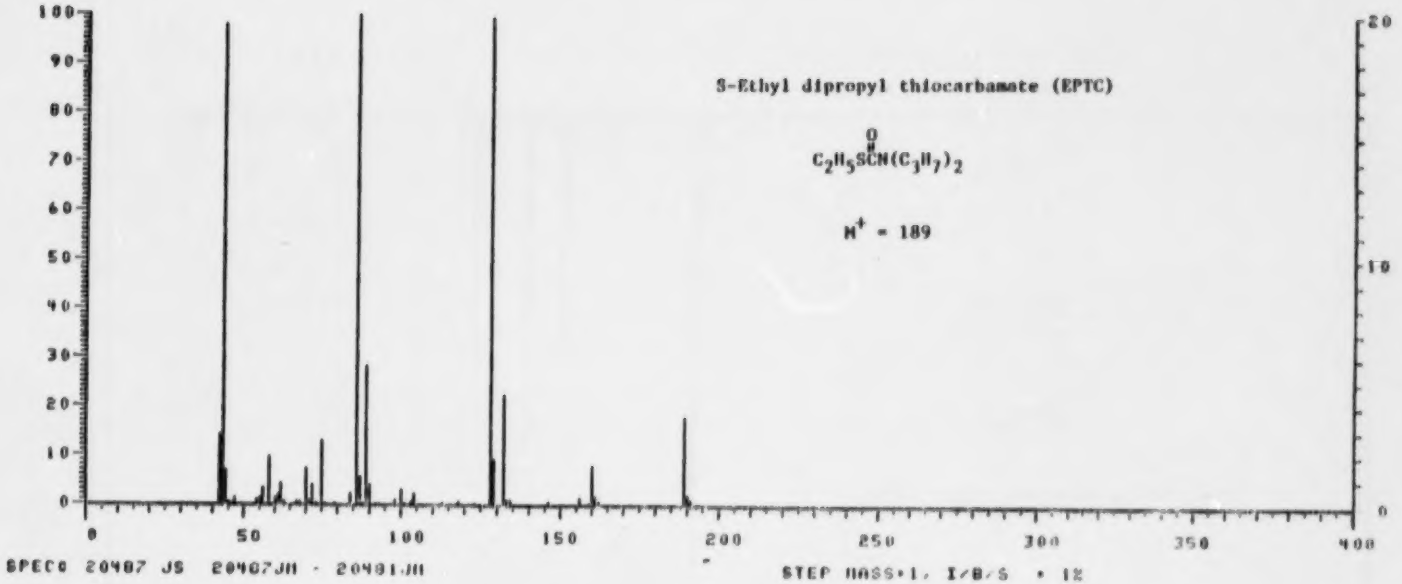

Figure B-22. Mass spectrum of S-ethyl dipropyl thiocarbamate (EPTC).

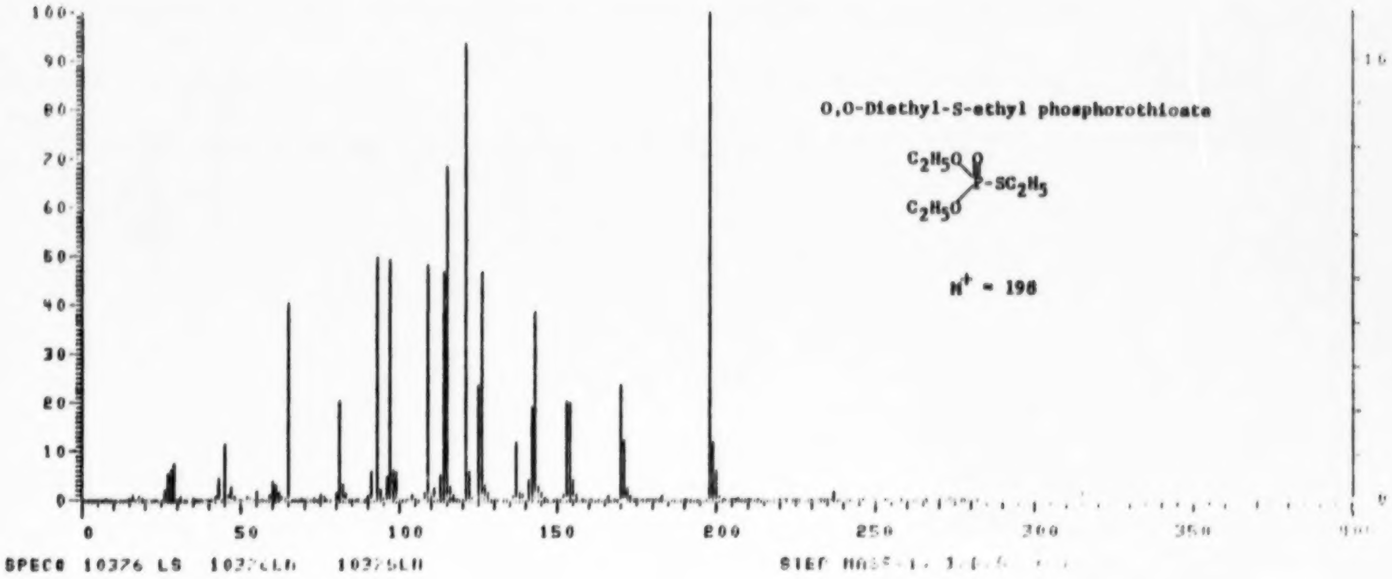

Figure B-23. Mass spectrum of O,O-diethyl-S-ethyl phosphorothioate.

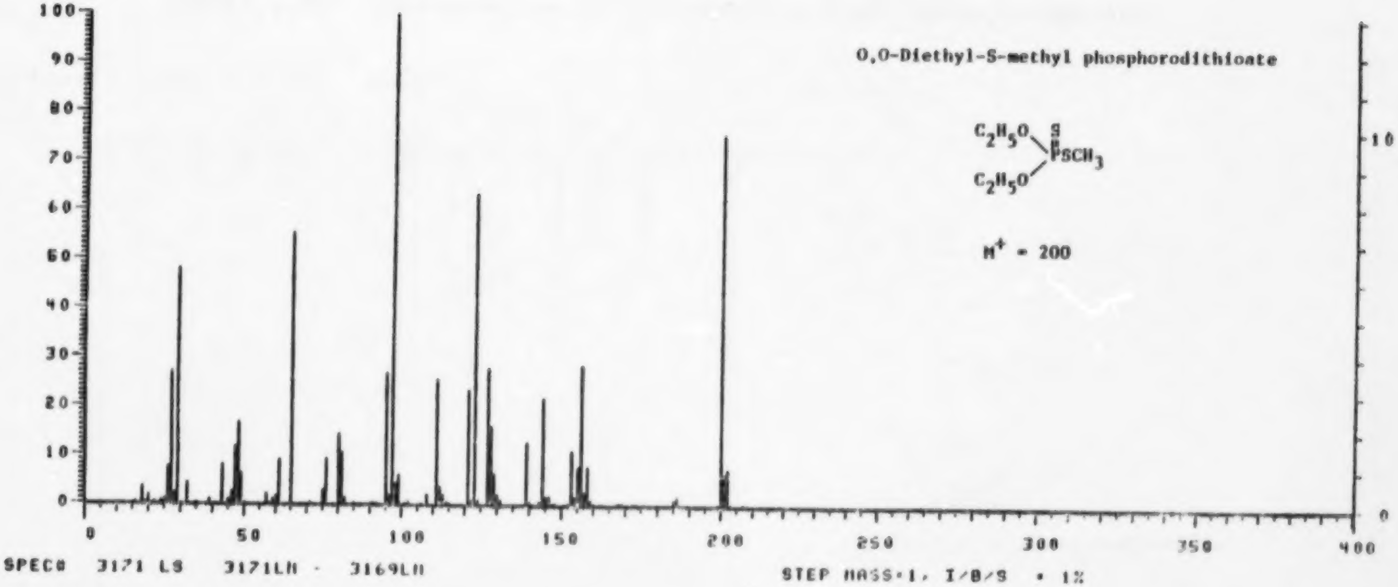

Figure B-24. Mass spectrum of O,O-diethyl-S-methyl phosphorodithioate.

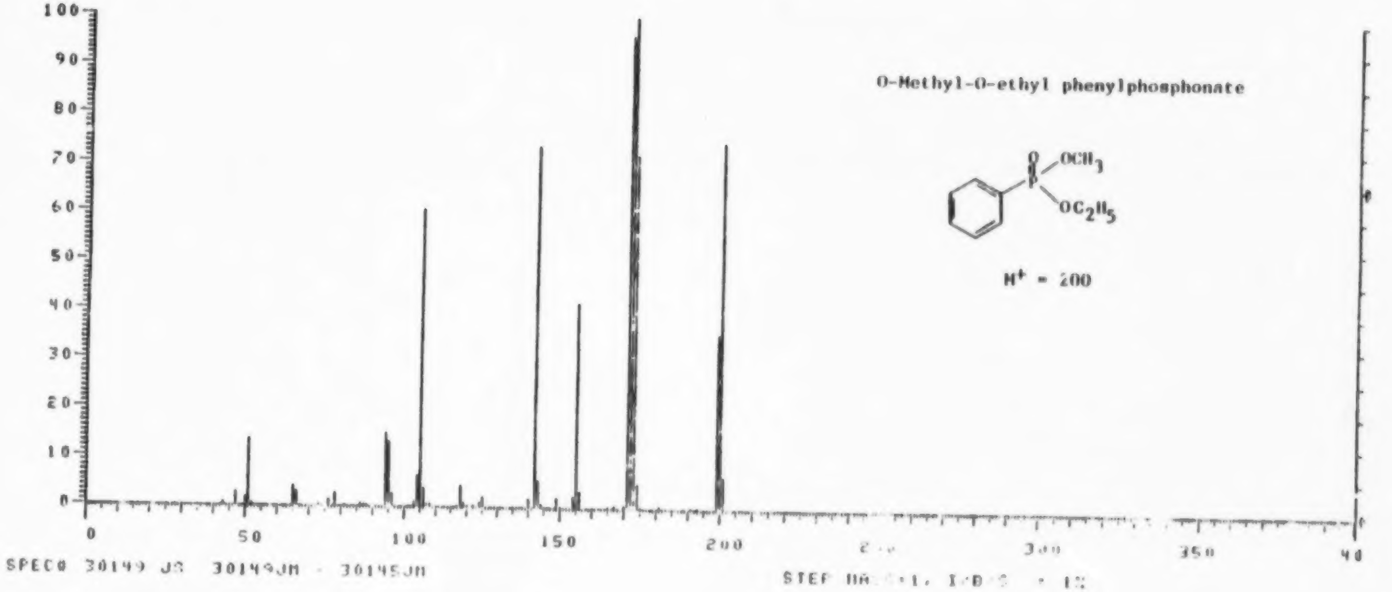

Figure B-25. Mass spectrum of O-methyl-O-ethyl phenylphosphonate.

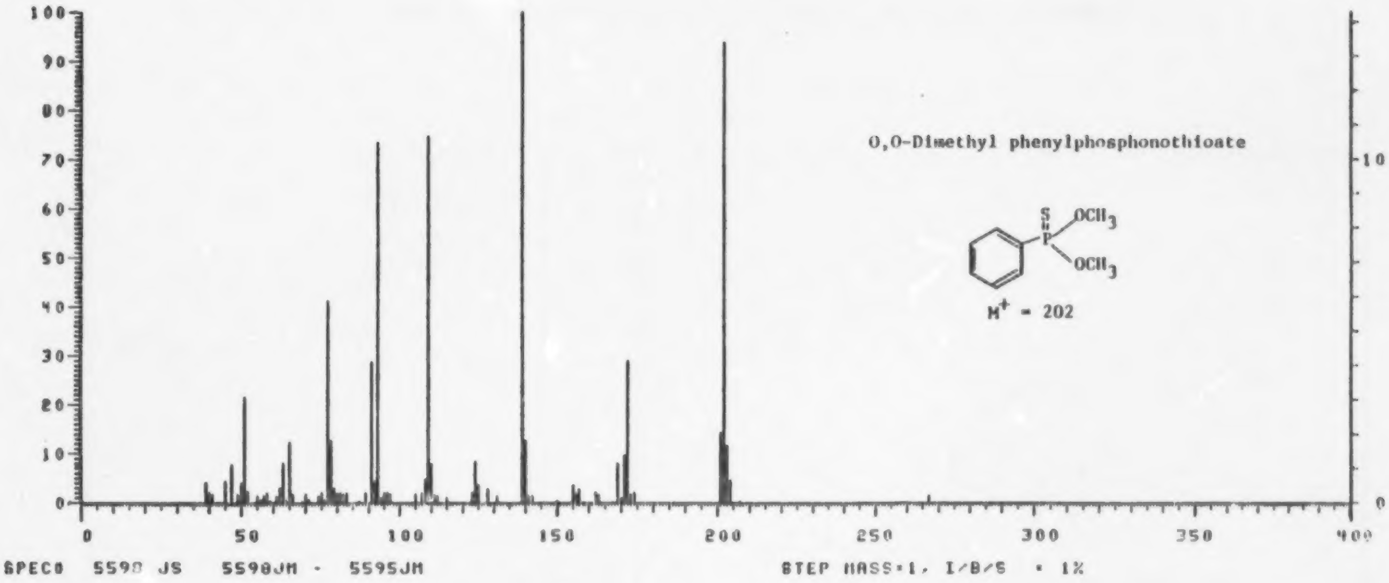

Figure B-26. Mass spectrum of O,O-dimethyl phenylphosphonothioate.

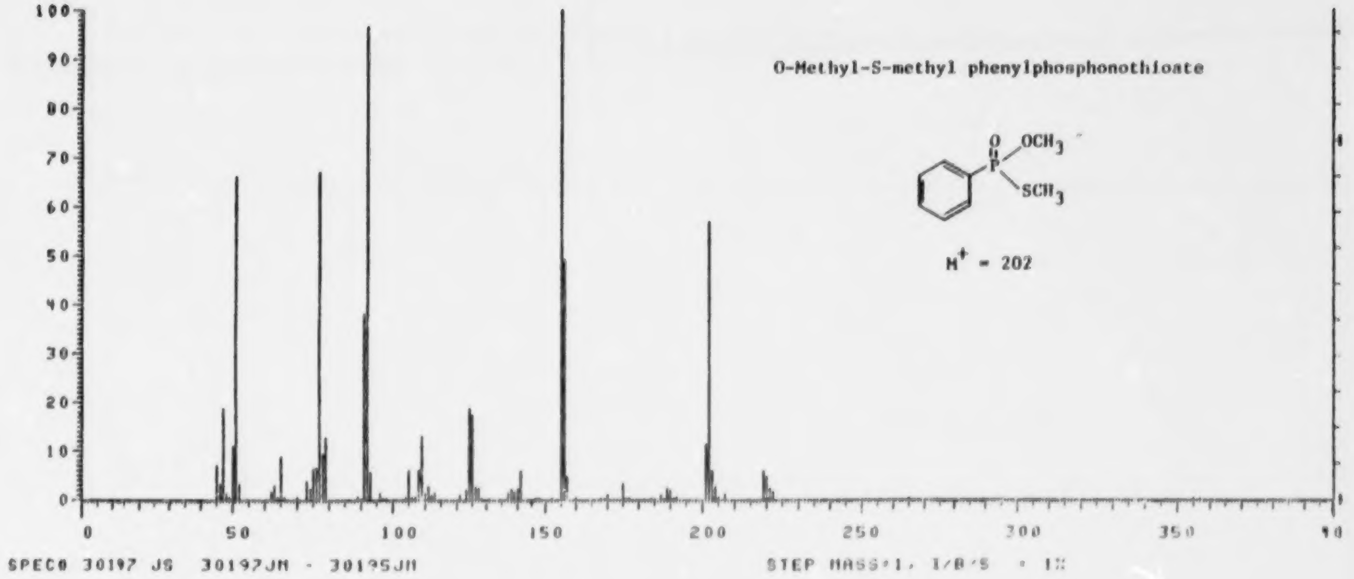

Figure B-27. Mass spectrum of O-methyl-S-methyl phenylphosphonothioate.

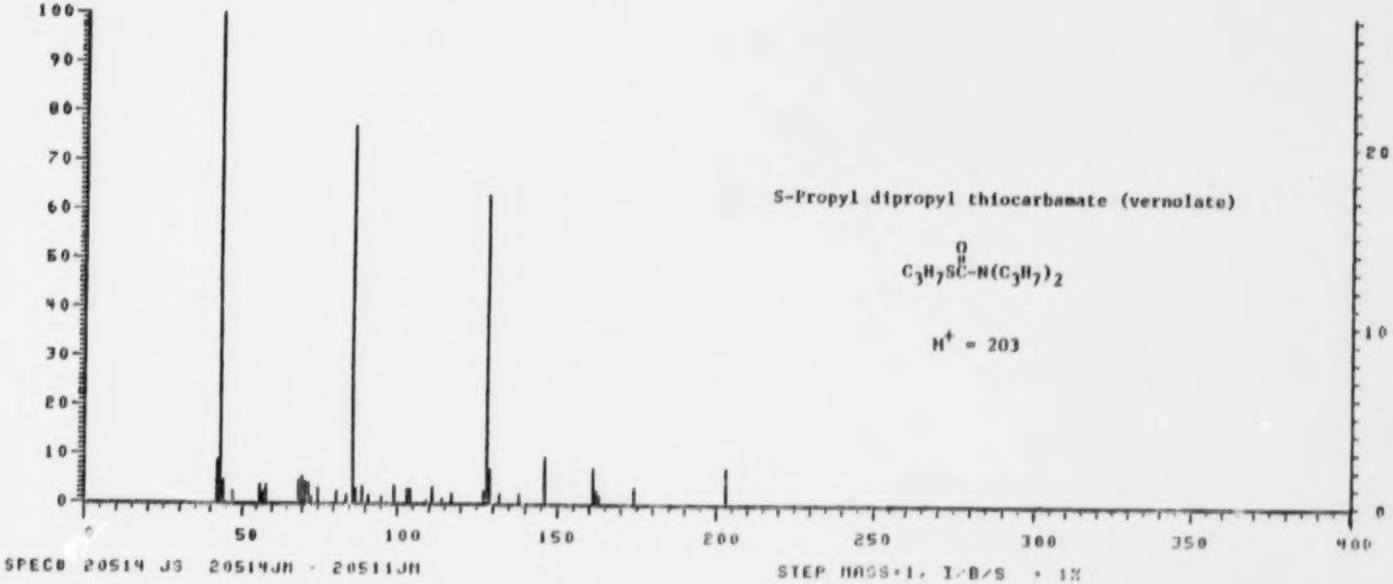

Figure B-28. Mass spectrum of S-propyl dipropyl thiocarbamate (vernolate).

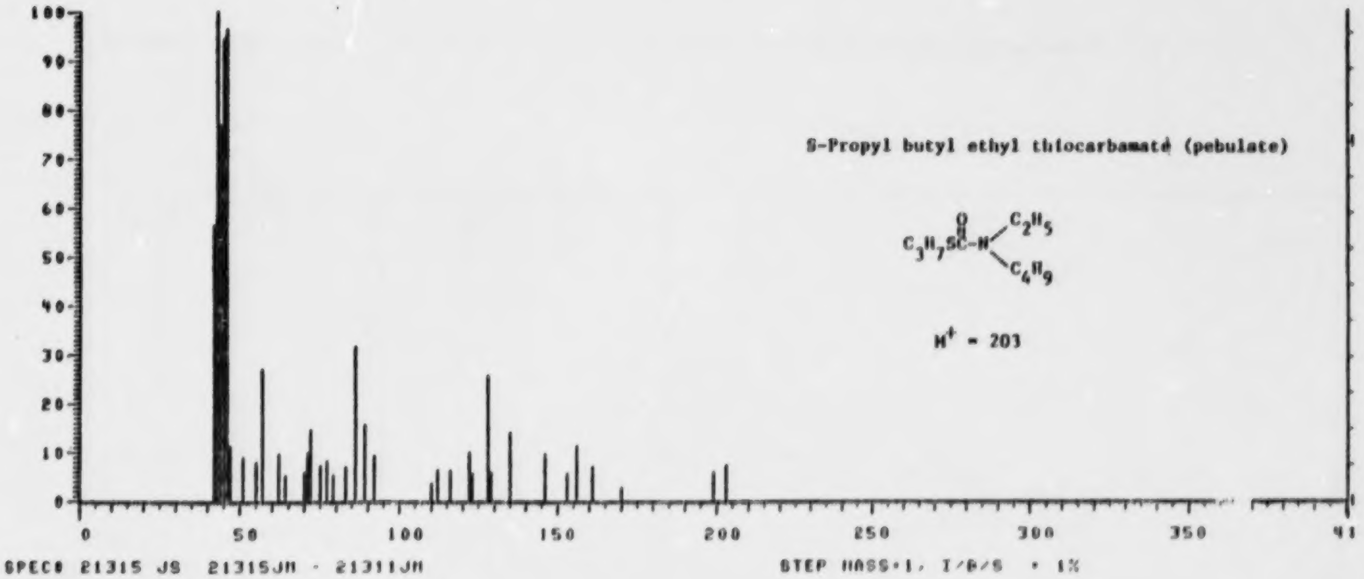

Figure B-29. Mass spectrum of S-propyl butyl ethyl thiocarbamate (pebulate).

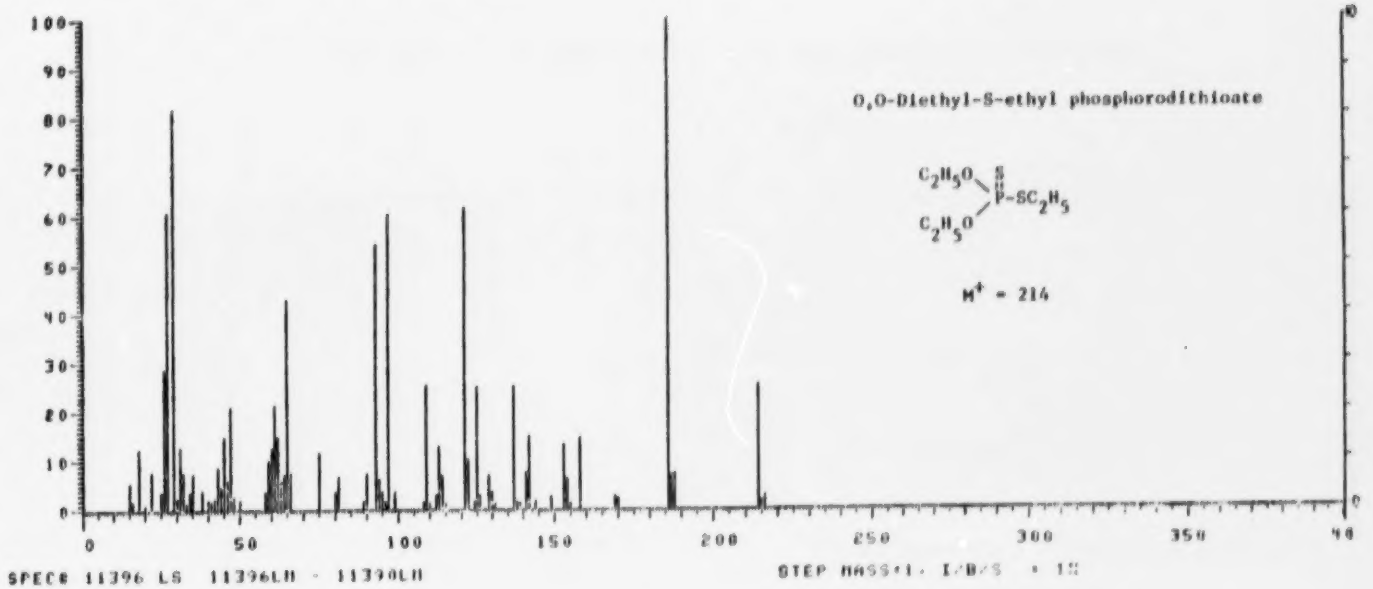

Figure B-30. Mass spectrum of O,O-diethyl-S-ethyl phosphorodithioate.

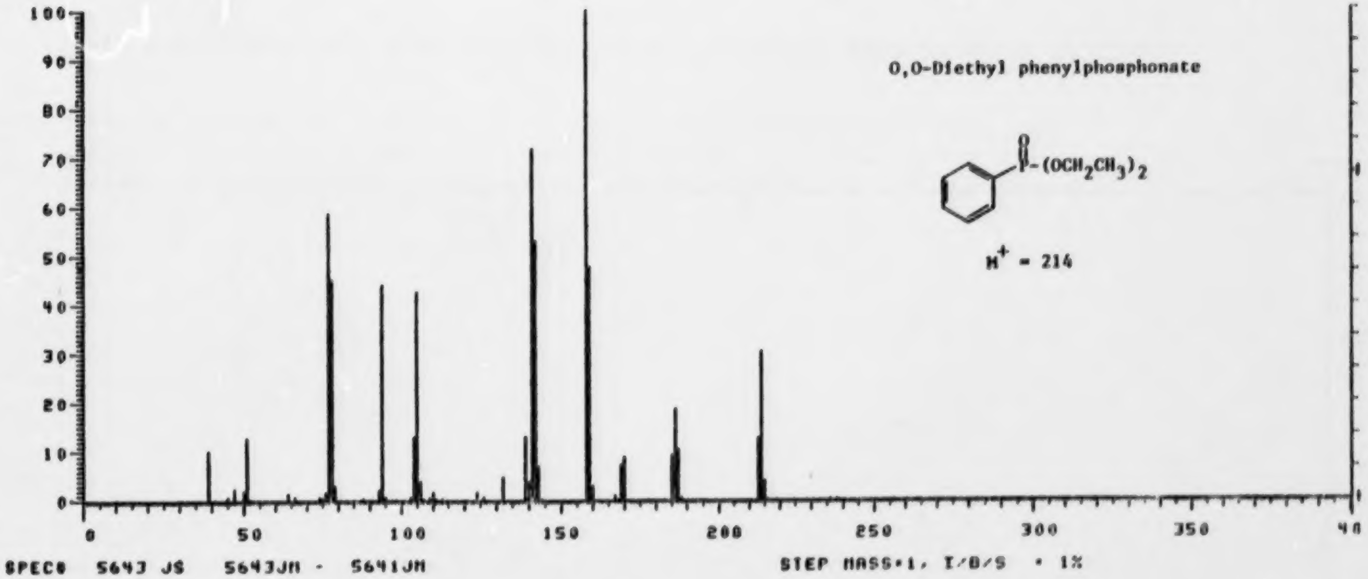

Figure B-31. Mass spectrum of O,O-diethyl phenylphosphonate.

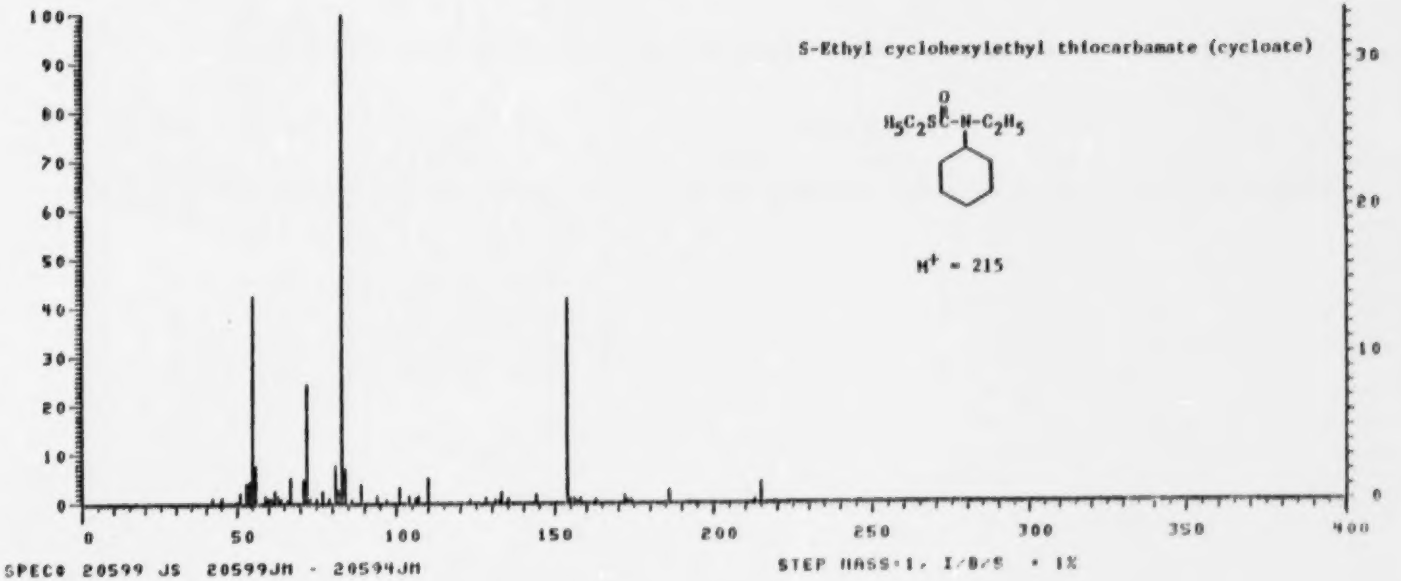

Figure B-32. Mass spectrum of S-ethyl cyclohexylethyl thiocarbamate (cycloate).

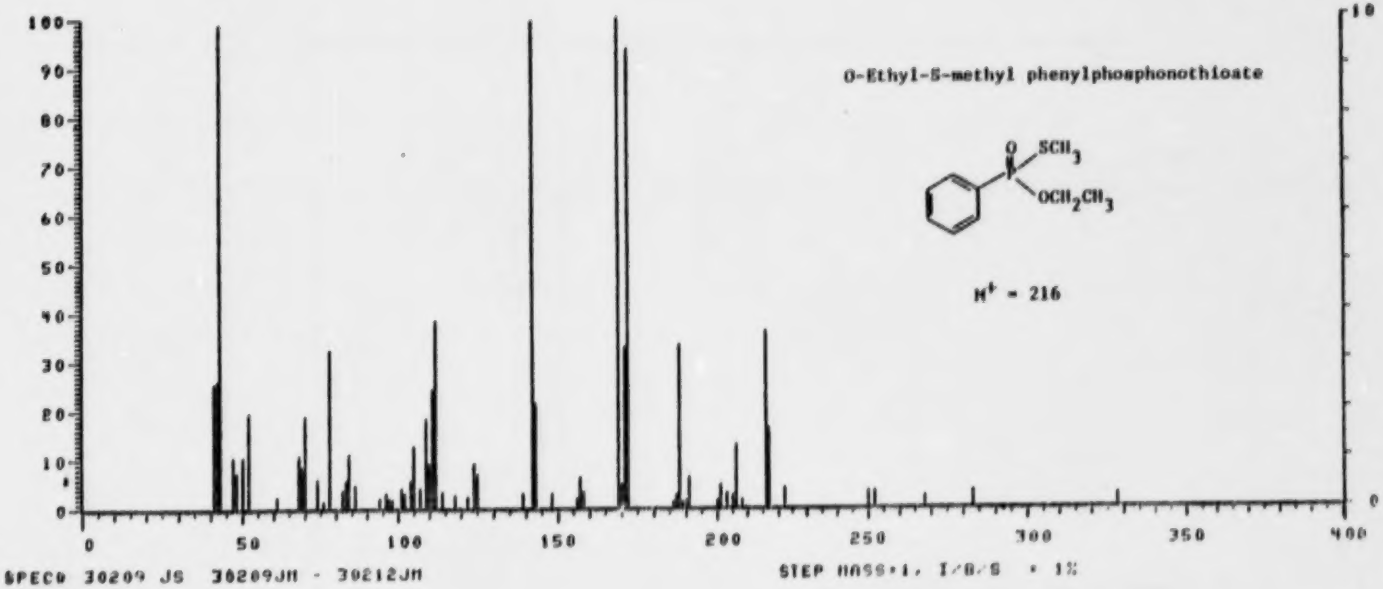

Figure B-33. Mass spectrum of O-ethyl-S-methyl phenylphosphonothioate.

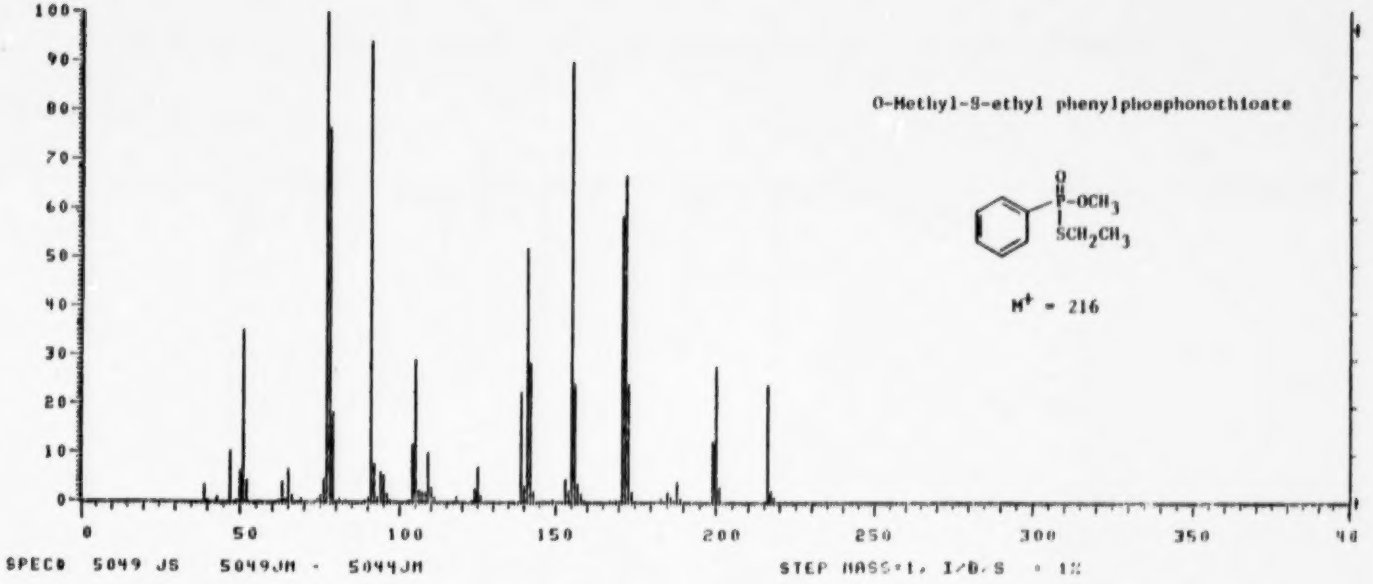

Figure B-34. Mass spectrum of O-methyl-S-ethyl phenylphosphonothioate.

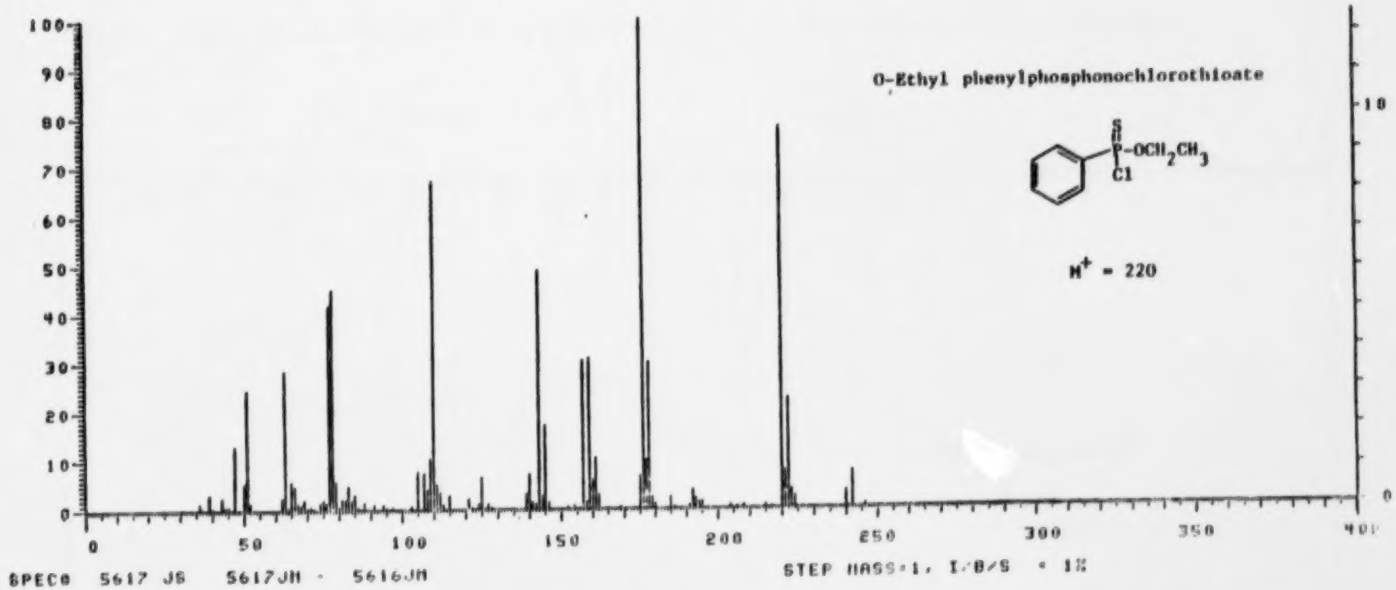

Figure B-35. Mass spectrum of O-ethyl phenylphosphonochlorothioate.

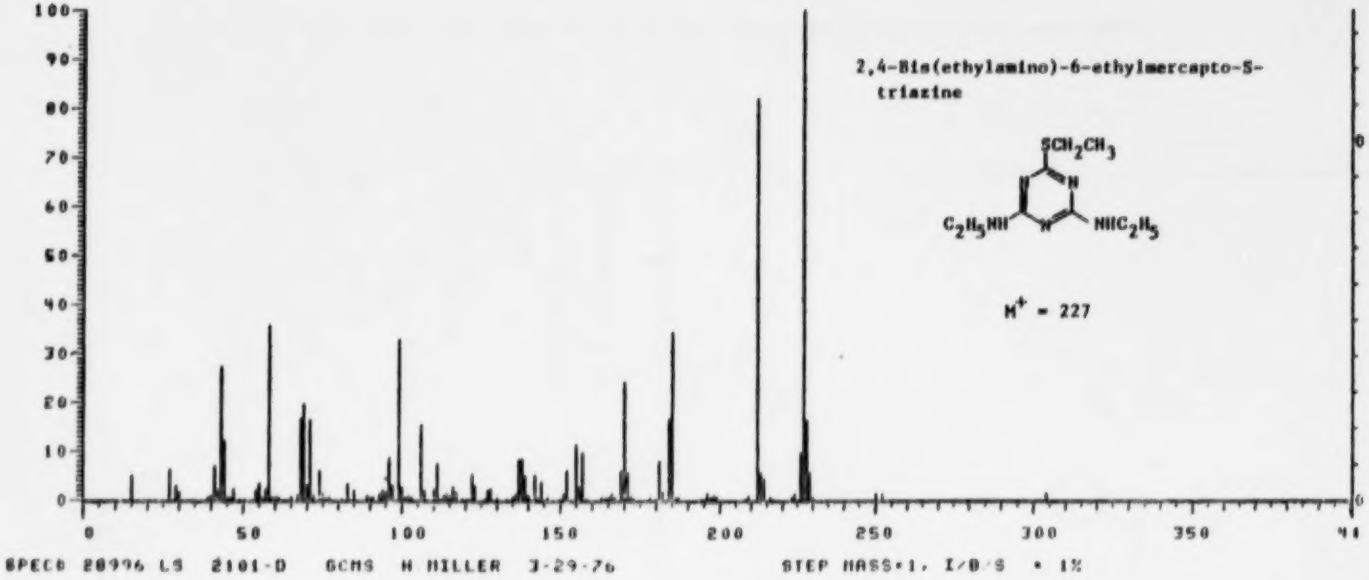

Figure B-36. Mass spectrum of 2,4-bis(ethylamino)-6-ethylmercapto-S-triazine.

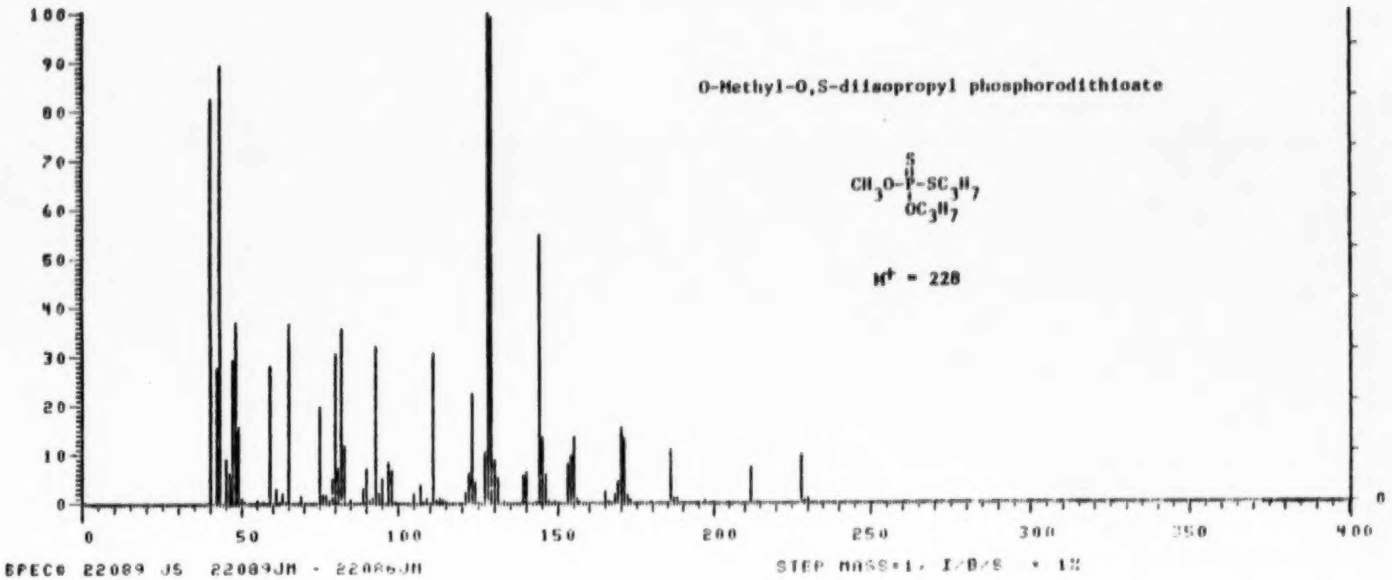

Figure B-37. Mass spectrum of O-methyl-O,S-diisopropyl phosphorodithioate.

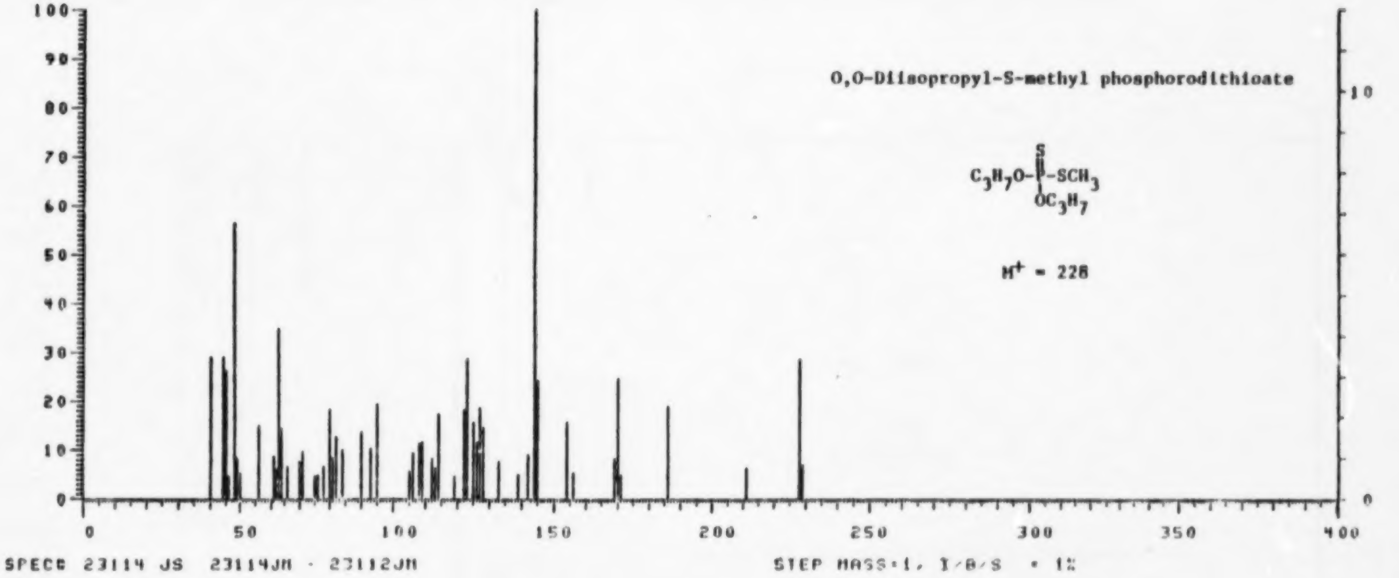

Figure B-38. Mass spectrum of O,O-diisopropyl-S-methyl phosphorodithioate.

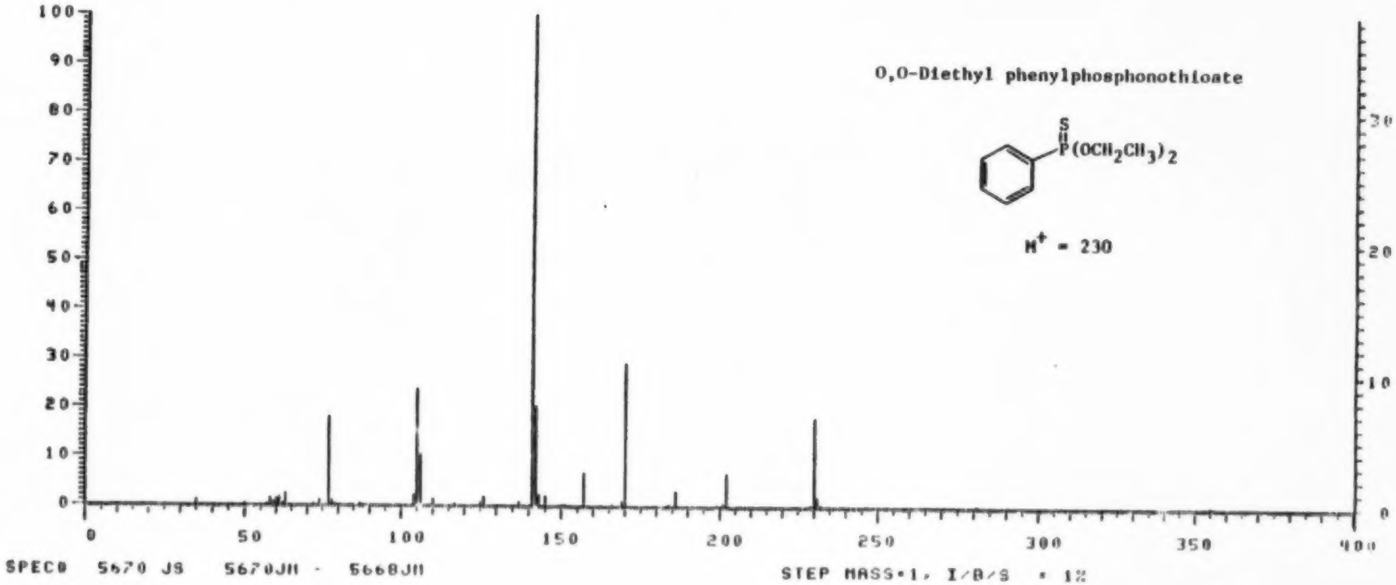

Figure B-39. Mass spectrum of O,O-diethyl phenylphosphonothioate.

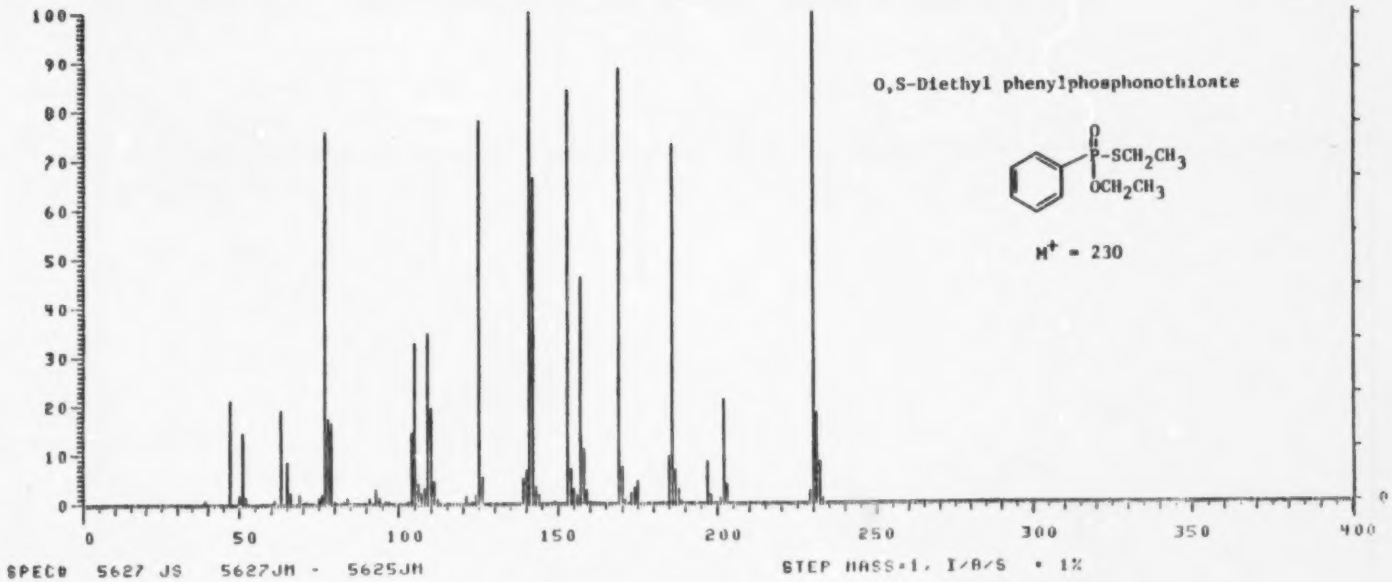

Figure B-40. Mass spectrum of O,S-diethyl phenylphosphonothioate.

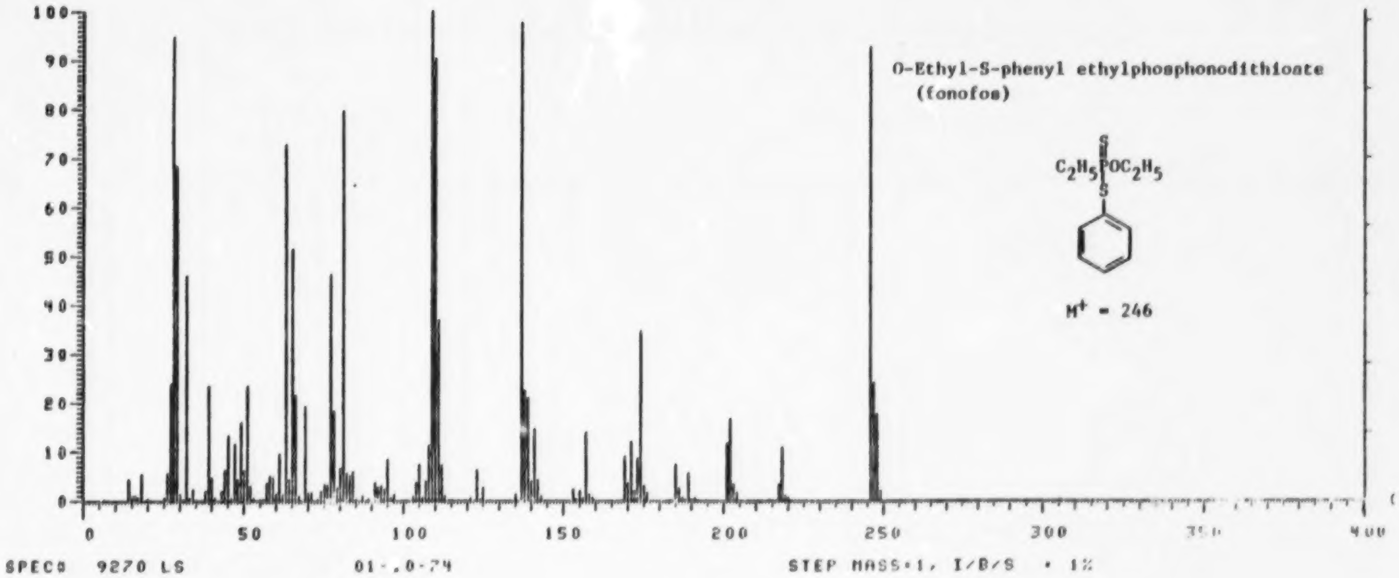

Figure B-41. Mass spectrum of O-ethyl-S-phenyl ethylphosphonodithioate (fonofos).

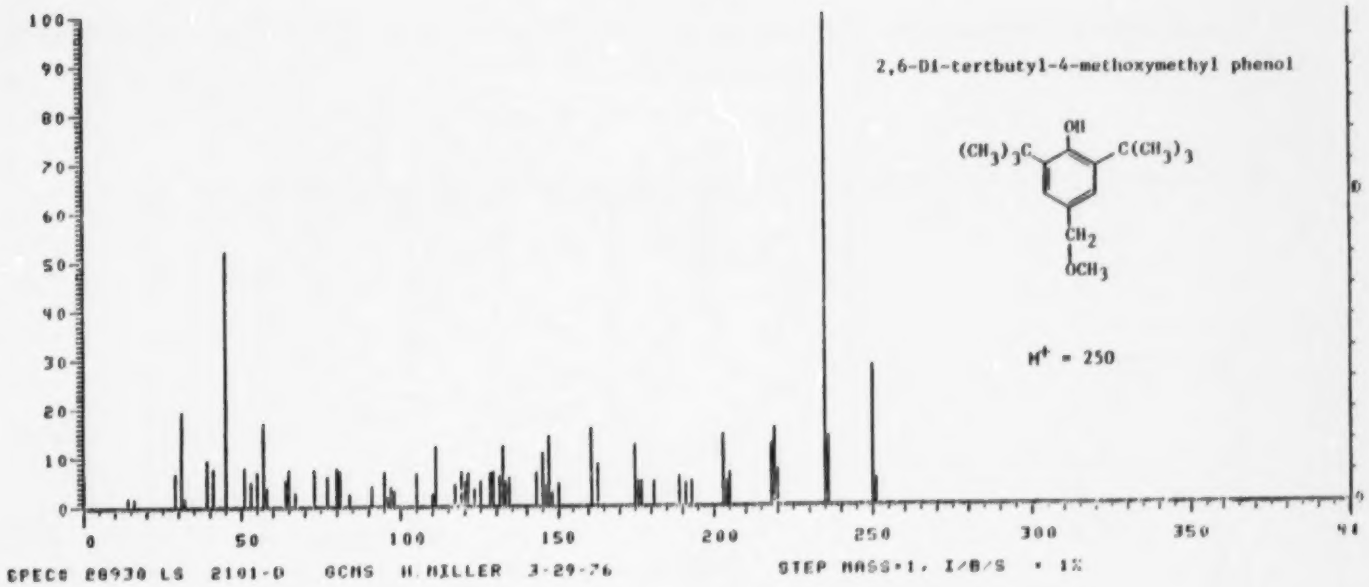

Figure B-42. Mass spectrum of 2,6-di-tertbutyl-4-methoxymethyl phenol.

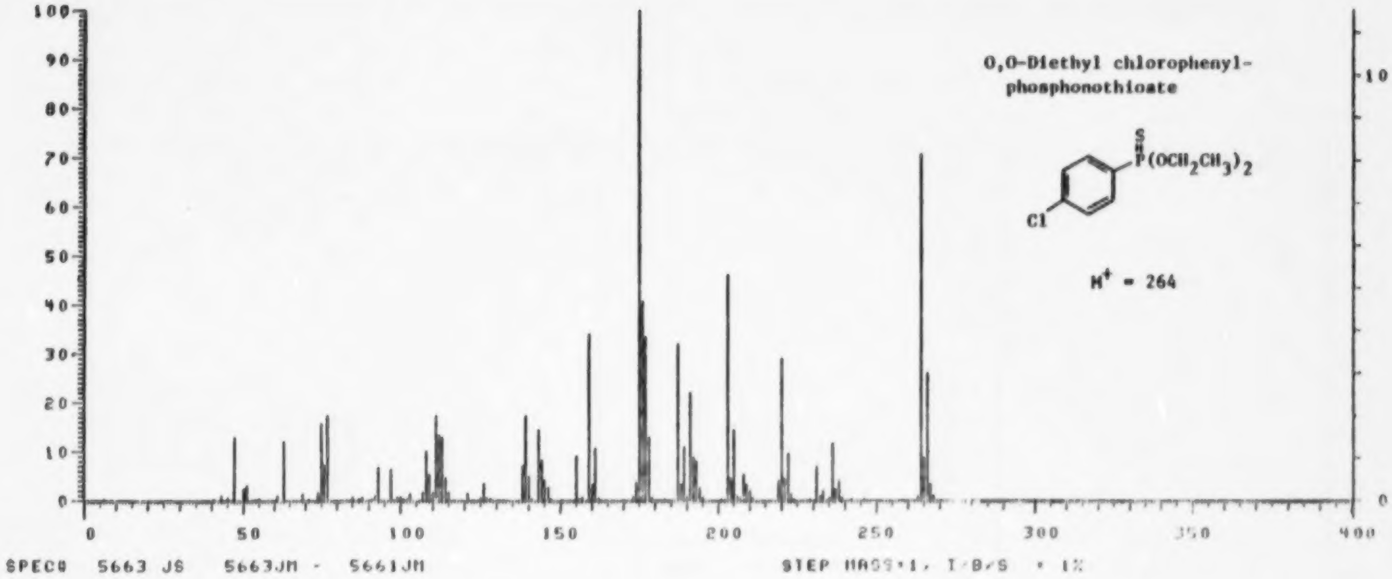

Figure B-43. Mass spectrum of O,O-diethyl chlorophenylphosphonothioate.

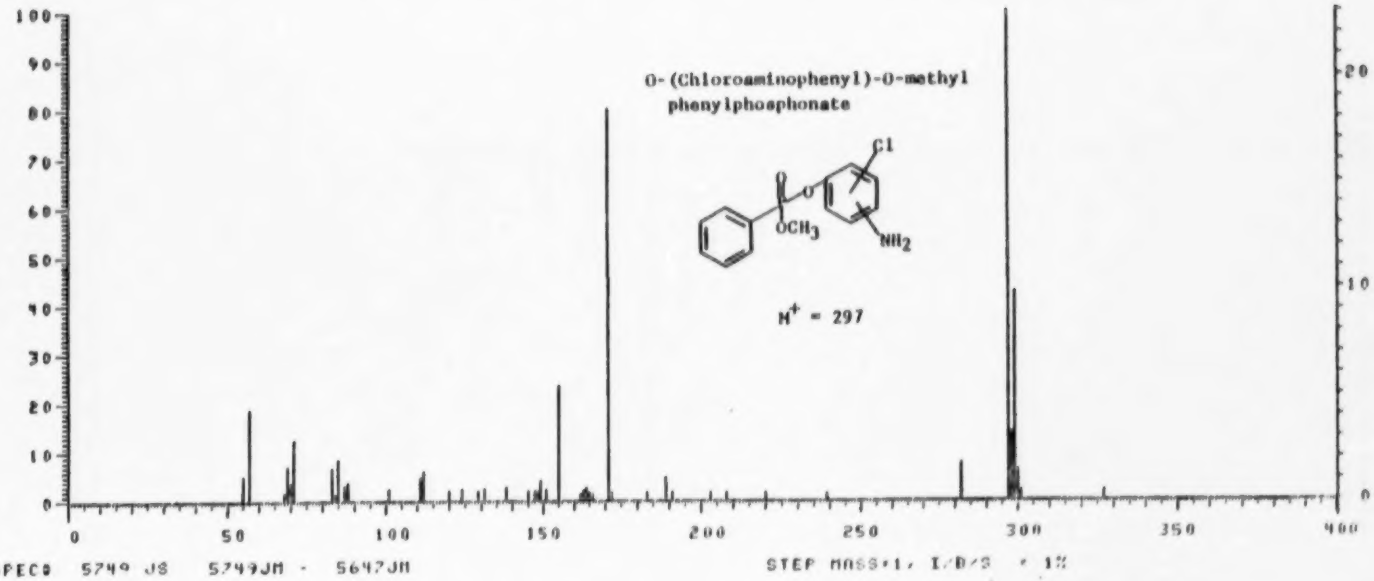

Figure B-44. Mass spectrum of O-(chloroaminophenyl)-O-methyl phenyl phosphonate.

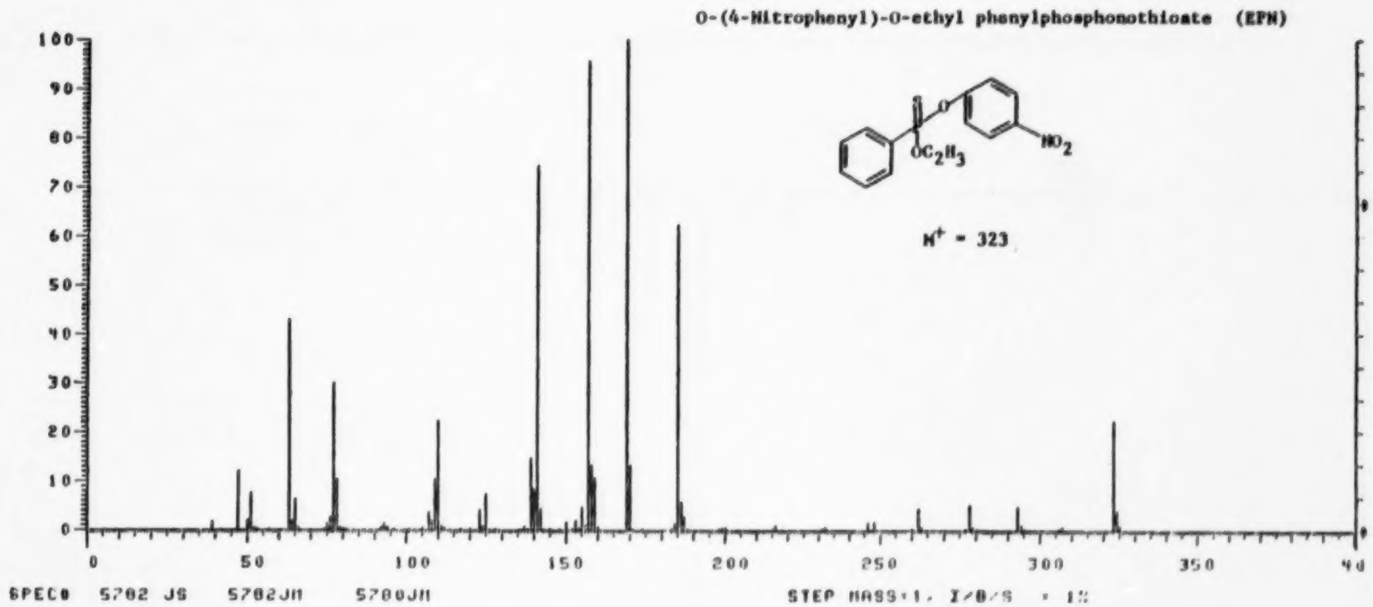

Figure B-45. Mass spectrum of O-(4-nitrophenyl)-O-ethyl phenylphosphonothioate (EPN).

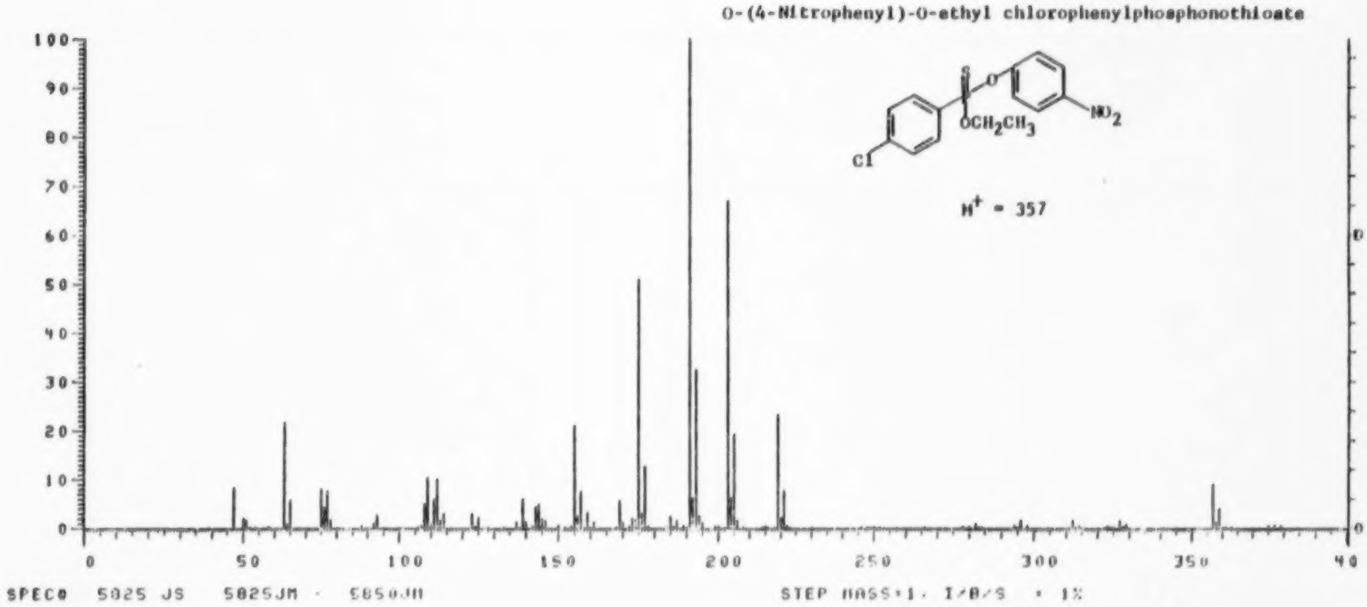

Figure B-46. Mass spectrum of O-(4-nitrophenyl)-O-ethyl chlorophenylphosphonothioate.

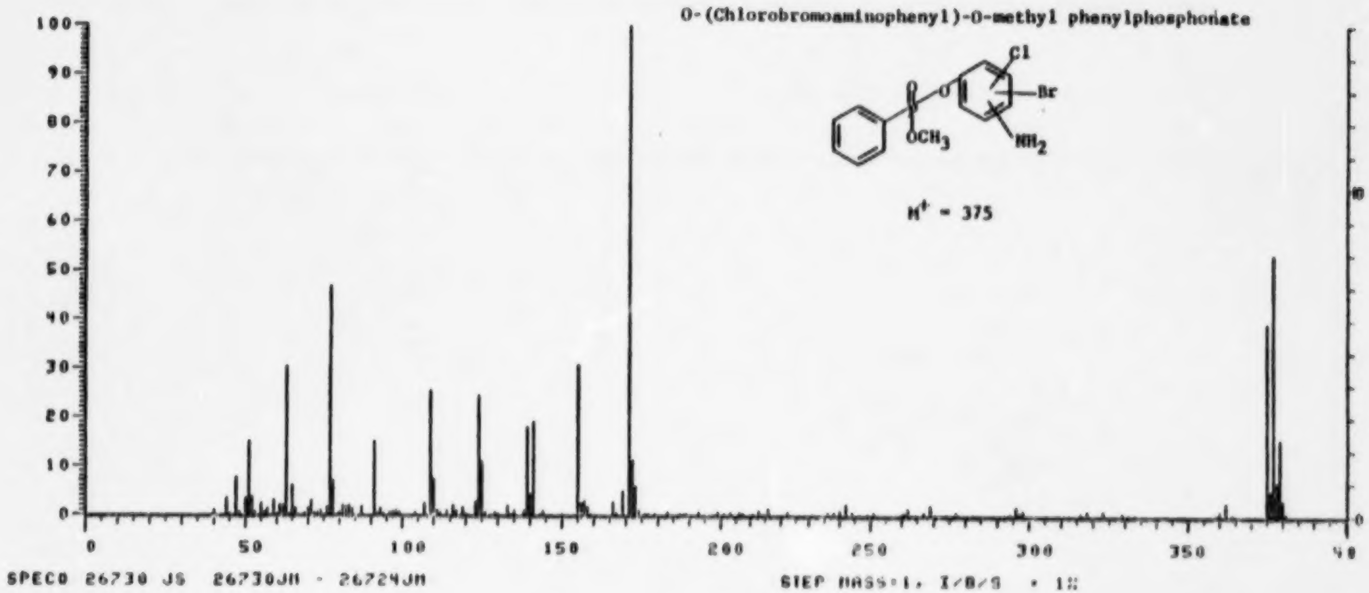

Figure B-47. Mass spectrum of O-(chlorobromoaminophenyl)-O-methyl phenylphosphonate.

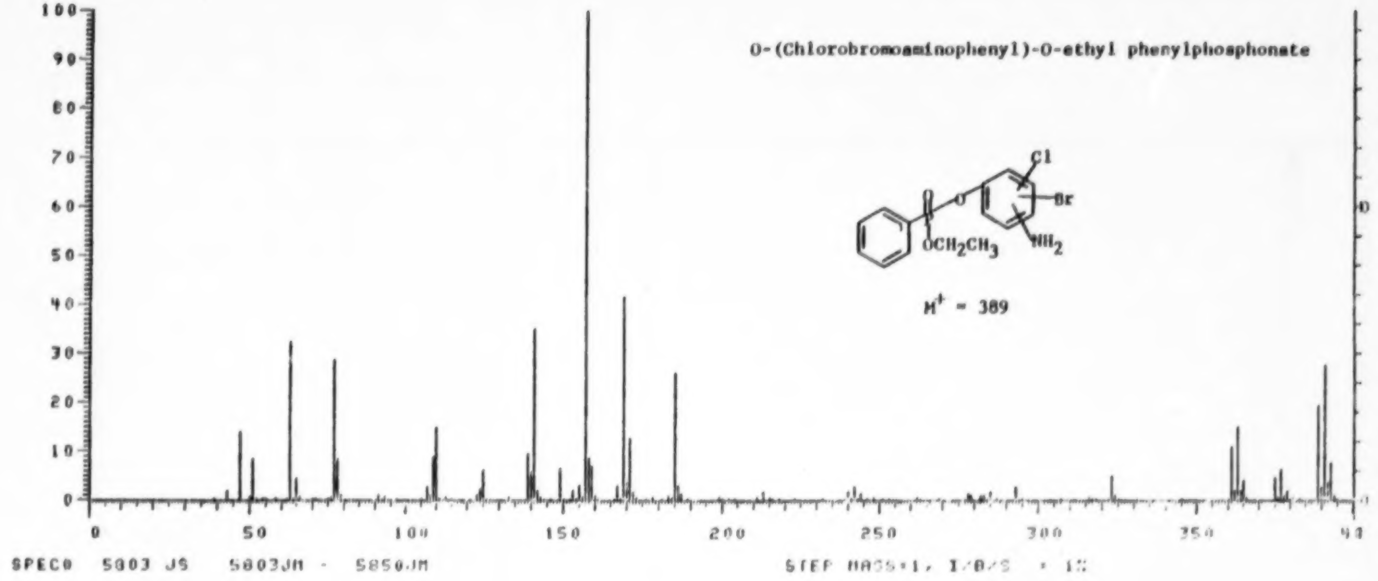

Figure B-48. Mass spectrum of O-(chlorobromoaminophenyl)-O-ethyl phenylphosphonate.